

OVERLOOKED SIGNIFICANCE OF CHROMIUM(V) AND CHROMIUM(IV) IN  
ENVIRONMENTAL CHEMISTRY AND INFLUENCE OF PEROXYACETIC ACID ON  
CHROMIUM IN WASTEWATER

A Thesis

by

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## ABSTRACT

Chromium (Cr) redox chemistry in the environment occurs through intermediate species penta-valent Cr (Cr(V)) and tetra-valent Cr (Cr(IV)) which are highly reactive. Environmental literature lacks substantial information on Cr(V) and Cr(IV) species in various redox processes. A perspective is first presented on the aquatic chemistry of Cr(V) and Cr(IV) and their behaviour under different environmental conditions. Following this, Cr-intermediate species were investigated in the reaction between Cr and peroxyacetic acid (PAA). Transition metal ions have been used to activate the disinfectant PAA for improved degradation of organic contaminants. The potential of Cr(III) already existing in water may react with PAA, producing radical species and Cr-intermediates that can oxidize coexisting contaminants in water. This research finds enhanced degradation of trimethoprim (TMP) and other pharmaceuticals from PAA-Cr(III) in basic pH. Reactive species present in this system are explored and implications of Cr(IV) and Cr(V) for future pollutant degradation are discussed.

## DEDICATION

This thesis is first dedicated to the Creator, YHWH, from whom I've received the innate ability to learn. Any fame or glory from this work belongs to Him, the Uncaused First-Cause, and Giver of all good things. I also dedicate this work to my parents and brothers that have supported me countless times and continue to love me regardless of my achievements.

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## CONTRIBUTORS AND FUNDING SOURCES

### **Contributors**

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# CHAPTER 1

## Overlooked role of chromium(V) and chromium(IV) in chromium redox reactions of environmental importance

### 1.1. Introduction

Heavy metals are known to pollute water resources and have both natural and anthropogenic sources. Anthropogenic sources of heavy metals consist of sewage discharge, pesticides, mine tailings, and coal combustion residuals, while natural sources of heavy metals can include soil erosion and weathering.<sup>1,2</sup> Industrial processes extracting metals may illegally discharge waste into the natural environment creating pollution events that need complete remediation.<sup>3</sup> Anthropogenic disturbances of geochemical processes can cause background levels of heavy metals to elevate and bioaccumulate, posing health risks to humans and the ecosystem because of their persistence in the environment and damage to the nervous system and other organs.<sup>4,5</sup> Among heavy metals, chromium (Cr) is a major pollutant, entering soil from waste of industrial activities such as coal-fired power generation, chrome pigment production, wood preservation, stainless steel production, galvanization, cement production, electroplating, and leather tanning.<sup>6-9</sup> Chromium has four isotopes in nature: isotopes <sup>50</sup>Cr, <sup>52</sup>Cr, <sup>53</sup>Cr, and <sup>54</sup>Cr having respective abundances of 4.35%, 83.79%, 9.50%, and 2.36%.<sup>10</sup>

The oxidation states of chromium ranges from -2 to +6. Three forms of Cr (Cr(0), Cr(III), and Cr(VI)) are thermodynamically stable and are extensively used in various industrial applications. The application of Cr(0) is in its metallic form (e.g., iron-based alloys such as stainless steel). Pollution from incineration of chrome materials results in small Cr(III)- and

Cr(VI)-containing particles, which may be inhaled through polluted air exposure and ultimately increase the levels of Cr in surface waters. Considering this and other pollution routes, Cr has been listed as a priority pollutant by the United States Environmental Protection Agency (USEPA) and is regulated in drinking water. The USEPA has set a Cr limit of 100 µg/L in drinking water. (<https://www.epa.gov/sdwa/chromium-drinking-water>)

In natural environments, most of Cr is present in Cr(VI) and Cr(III) species and their concentrations depend on the total concentration of Cr, pH and pε of water (Fig. 1.1).<sup>11</sup> The oxyanions of Cr(VI) (i.e., Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and HCrO<sub>4</sub><sup>-</sup>) are dominant species between pH 0.0 and 6.0. Other oxyanion of Cr(VI), CrO<sub>4</sub><sup>2-</sup> appears at pH ~ 4.5 with maximum concentration at pH ≥ 8.0. Comparatively, there are five species of Cr(III) present in water (Cr<sup>3+</sup>, CrOH<sup>2+</sup>, Cr(OH)<sub>2</sub><sup>+</sup>, Cr(OH)<sub>3</sub><sup>0</sup>, and Cr(OH)<sub>4</sub><sup>-</sup>).<sup>12</sup> The values of redox potential (i.e., pε) and pH provide information for which of the equilibrium species of Cr exist in the water. Insoluble at neutral pH, Cr(III) is the most thermodynamically stable and kinetically inert.<sup>13</sup> The Cr(III) ion exists in a hydration sphere as the hexaquo ion [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> (pK<sub>a</sub> = 4.0), with each water molecule being hydrogen bonded to two other water molecules in a second sphere.<sup>14,15</sup> The speciation of Cr(III) as a function of pH is presented in Fig. 1.2.<sup>12</sup> The Cr species in an acidic medium is Cr(III), whereas Cr(OH)<sub>3</sub><sup>0</sup> and Cr(OH)<sub>4</sub><sup>-</sup> are main Cr species in alkaline conditions (Fig. 1.2).<sup>12</sup>

Chromium(III) has also been known as an essential micronutrient for humans; however, the molecular mechanisms are still unclear, bringing into question how essential its supplementation is.<sup>14</sup> Some studies regard Cr(III) supplementation as beneficial in weight loss for patients with diabetics, while others postulate that excessive intake could be carcinogenic.<sup>16</sup> Concerns over potential oxidation of Cr(III) supplements to Cr(VI) rise from physiological variation in pH, redox potential, and occurrence of oxidizing compounds. The Food and Nutrition Board of the National



Academics of Sciences, Engineering, and Medicine has set adequate intake values of Cr(III) at 25 µg/day and 35 µg/day for women and men, respectively, far less than provided by chromium supplementation.<sup>16</sup> The World Health Organization has set an upper limit of safe intake of Cr at 250 µg/day; excessive Cr(III) intake is unwarranted at this time because of studies revealing toxicity of Cr(III) at high concentrations.<sup>17</sup> For example, the popular Cr(III) supplement known as chromium picolinate (Cr(pic)<sub>3</sub>) has shown clastogenic, cytotoxic, and chromosome damage to Chinese hamster ovary cells with other short-term tests that have revealed deoxyribonucleic acid (DNA) damage.<sup>18,19</sup> Yet, other studies have shown no genotoxic effects in physiological conditions, including a chronic study on rats and mice revealing no toxicity of Cr(pic)<sub>3</sub>.<sup>19,20</sup> One reason for the apparent discrepancy in toxicity could be due to the low cellular uptake of Cr(III).<sup>20</sup> Significantly, Cr(VI), but not Cr(III) has been reported to have potential effects of cancers to humans.<sup>7,21</sup> Therefore, more stringent regulations in the State of California have even set Cr(VI) limits in drinking water to 10 µg/L.<sup>22</sup>

The toxicity of Cr(VI) is potentially related to the production of reactive intermediates Cr(V) and Cr(IV) under biological environments. In earlier research, the presence of Cr(V) and Cr(IV) was largely ignored. However, detection of Cr(V) with ligands such as thiols, glycols, and phenols has led to elegant publications including reviews, especially since the finding that the Cr(V) species are capable of damaging DNA.<sup>14,23,24</sup> Reduction of Cr(VI) to Cr(V) and subsequently to Cr(III) is an intercellular reduction process, possibly carried out by nicotinamide adenine dinucleotide (NADH) and/or nicotinamide adenine dinucleotide phosphate (NADPH).<sup>25</sup> Other intercellular reducing agents include cysteine, lipoic acid, fructose and ribose, as well as redox proteins such as cytochrome P450 and hemoglobin.<sup>14</sup> Under physiological conditions, the reduction of Cr(VI) by ascorbate and glutathione that occurs within cells can also produce reactive

oxygen species (ROS) such as singlet oxygen ( $^1\text{O}_2$ ), superoxide radical ( $\text{O}_2^{\bullet-}$ ), hydroxyl radical ( $\bullet\text{OH}$ ), and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) that can damage DNA.<sup>25,26</sup>

Though ROS have shown to play a role in Cr(VI)-induced oxidative stress, the direct relationship between DNA-ROS and Cr(VI)-induced DNA damage is still debated.<sup>14</sup> For example, a tetraperoxo-chromate(V) species has been suggested in the reduction of Cr(VI) by  $\text{H}_2\text{O}_2$ , forming ROS like  $\bullet\text{OH}$  that resulted in DNA damage; yet, another study disproved the generation of  $\bullet\text{OH}$  in this system using an electron paramagnetic resonance (EPR) technique.<sup>14</sup> Additionally, cytotoxicity, genotoxicity, chromosomal aberrations, and DNA lesions which might lead to carcinogenesis can occur from the reactions of ROS and Cr(V)/Cr(IV).<sup>26</sup> Also worth mentioning is that Cr(VI) can form complexes with biological thiols which has been determined by various spectroscopic techniques.<sup>27</sup> The potential cellular mechanisms involving Cr intermediates is illustrated in Fig. 1.3.

The mechanisms involving Cr-induced carcinogenicity depend on multiple factors including cell type, DNA adduct and free radical formation, Cr(VI) concentration, and reactivity of Cr-intermediates.<sup>28</sup> Though Cr(V) and Cr(IV) might be grouped together as reactive Cr intermediates, their function in toxicity differs. For example, both Cr(V) and Cr(IV) were shown to induce DNA double-strand breaks, yet Cr(IV) had more mutation frequencies in the hypoxanthine phosphoribosyltransferase (HPRT) gene compared to Cr(V).<sup>29</sup> More research is needed not only to identify specific mechanisms of Cr-induced carcinogenicity, but also the role of intermediates Cr(V) and Cr(IV). Selective detection of Cr(V) has been shown by EPR and UV-visible measurements, electrospray mass spectrometry (ES-MS), and X-ray absorption spectroscopy methods.<sup>24,30-32</sup> Additionally, kinetics data on the interaction of Cr(VI) with reducing agents *L*-cysteine, glutathione, *L*-ascorbic acid, and Trolox using stopped-flow UV-visible

spectrophotometry have been obtained to gain insight into the information of Cr(V) and Cr(IV) species.<sup>33</sup> Intermediates Cr(V) and Cr(IV) are often responsible for multiple roles in Cr-induced toxicity.

To date, great progresses have been made on the Cr(V) and Cr(IV) species due to their biological importance, but their roles in the environmental processes are largely overlooked. Significantly, these reactive species of Cr (i.e., Cr(V) and Cr(IV)) are likely produced from the interaction of Cr(VI) with natural organic ligands (or compounds) and the reaction of Cr(VI) with reducing moieties of natural organic matter (NOM), as well as from the interaction of Cr(III) with oxidants. The focus of this review is thus providing the basic properties and characterization of Cr(V) and Cr(IV) to bring attention to researchers for the need to carry out more mechanistic investigations to shed light on the species involved in the redox reactions of chromium in environmental processes. The summary of information is presented in the next section, followed by examples of studies on chromium of environmental importance.

## **1.2. Chromium(V) and chromium(IV) species**

Cr(V) and Cr(IV) species are highly reactive intermediates. This may largely be attributed to the higher standard redox potentials of Cr(V) and Cr(IV) species than Cr(VI) in acidic conditions (Fig. 1.4).<sup>14,34</sup> Cr(VI) is expected under oxidizing conditions, completely soluble across the pH range, and highly mobile overall.<sup>6,13,14</sup> The one-electron redox potential under acidic conditions decrease in the order as Cr(IV) > Cr(V) > Cr(VI). The chemical properties of Cr(V) and Cr(IV) are different from those of Cr(VI) and Cr(III). The redox potentials of Cr(V) and Cr(IV) are not available in alkaline conditions. High-valent Cr species (i.e., Cr(VI), Cr(V), and Cr(IV)) are

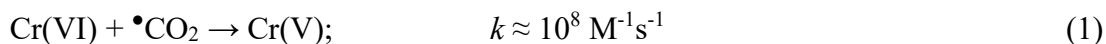
powerful oxidants. Comparatively, Cr(II) is a good reductant (see the negative redox potential of Cr(II)/Cr(0) in Fig. 1.4).<sup>14,34</sup>

Both Cr(V) and Cr(IV) are typically short-lived, making them often challenging to quantify. Both the Cr species could be stabilized by complexing agent 2-ethyl-2-hydroxybutanoate (ehba) and UV-visible spectra were obtained (Fig. 1.5).<sup>14</sup> All Cr species have characteristic spectra to distinguish different high-valent Cr species. In the UV range, the Cr(V) complex has reasonable molar absorptivity ( $\epsilon \sim 10^3 \text{ M}^{-1}\text{cm}^{-1}$ ). The Cr(IV) complex also absorbs over a wide wavelength range with a maximum near 350 nm ( $\epsilon \sim 1.7 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ ). Cr(III) forms a weak complex with ehba (Fig. 1.5).<sup>14</sup> The spectrum of Cr(VI) represents the maximum molar absorptivity of  $\text{HCrO}_4^-$  at a different wavelength.

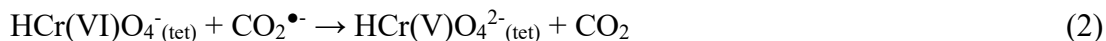
The EPR technique is often applied in detecting Cr(V) species. The typical EPR spectra of Cr(V) complex species for hydroxamate complexing agents are given in Fig. 1.6.<sup>35</sup> The hydroxamate groups are likely moieties in humic substances and interact with Cr(VI) to form Cr(V)-hydroxamate species.<sup>36,37</sup> The EPR spectra for the Cr(V) complexes have a center at  $g_{\text{iso}} \approx 1.98$  with a strong narrow line.<sup>38</sup> Another example is the reduction of Cr(VI) by catecholamines to produce octahedral Cr(V) species which has been quantified by EPR yielding a signal at  $g_{\text{iso}} \sim 1.972$  ( $A_{\text{iso}}(^{53}\text{Cr}) > 23.9 \times 10^{-4} \text{ cm}^{-1}$ ).<sup>30</sup> Many other Cr(V) complexes with EPR signals obtained include Cr(V)-ascorbate, Cr(V)-D-glucose, and Cr(V) with D-ribose 5'-monophosphate.<sup>38</sup> Interestingly, diol ligands might play an important role in stabilizing Cr(V) complexes which has been noted by detection of Cr(V) EPR signals after 48 hours of reaction.<sup>38</sup> The Cr(V)-glutathione (GSH) complex ( $[\text{Cr(V)O}(\text{LH}_2)_2]^{3-}$  ( $\text{LH}_5 = \text{GSH}$ )) has been characterized and quantified by electrospray mass spectrometry, X-ray absorption, EPR spectroscopy, and other analytical techniques.<sup>31</sup>

Since Cr(IV) complexes are less stable in aqueous solution than Cr(V) complexes and EPR spectroscopy technique cannot be used for Cr(IV) complexes under ambient conditions, less is known about Cr(IV) chemistry.<sup>38</sup> Several studies have investigated Mn(II) as a selective trap for Cr(IV), but that has been overall inconclusive in determining the role of Cr(IV) in DNA damage.<sup>38</sup> In other conditions, the fast reaction between Cr(III) and  $\bullet\text{OH}/\text{SO}_2\bullet^-$  at acidic conditions revealed a Cr(IV) spectrum between 250 and 420 nm with an increasing molar absorption coefficient from 4.3 to 48  $\text{M}^{-1}\text{cm}^{-1}$ , ultimately producing Cr(VI).<sup>14</sup>

The pulse radiolysis technique was applied to produce Cr(V) from Cr(VI). The reaction of Cr(VI) with  $\bullet\text{CO}_2$  under nitrous oxide saturated solution generate Cr(V) (eq. 1).



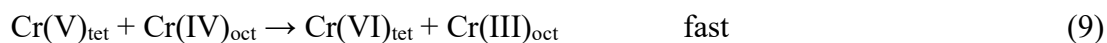
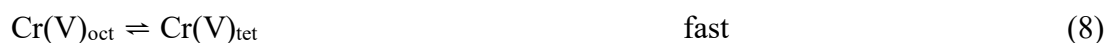
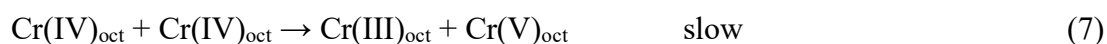
The reaction (1) was performed at different pH and the spectra of obtained Cr(V) and Cr(IV) are presented in Fig. 1.7.<sup>39</sup> In the pH range from 1.85 to 4.75, the spectrum of Cr(V) had no variation.<sup>39</sup> The molar absorptivity of Cr(V) was lower in acidic pH range compared to that in the alkaline pH range. The spectra of Cr(V) did not change significantly in the pH range from 8.0 to 13.7.<sup>39</sup> The decay of Cr(V) in aqueous solution has been proposed based on the disproportionation of Cr(V) as a function of pH and conductivity measurements, which could be described by reactions (2) – (6).





The constants of protonic equilibria of reactions (3), (4), and (6) suggest that both mono-protonated and de-protonated species of Cr(V) co-exist at pH 7.0 (Fig. 1.8).<sup>39</sup>

It has been proposed that octahedral Cr(IV) complexes can slowly react with each other, producing Cr(III) and Cr(V) octahedral coordination, as seen in eq. 7.<sup>14</sup> Subsequently, the fast rearrangement of Cr(V) octahedral to tetrahedral complexes allows for a rapid reaction between Cr(V) tetrahedral and Cr(IV) octahedral complexes which form Cr(VI) and Cr(III) as shown in the following eqs. 8 and 9.<sup>14</sup>

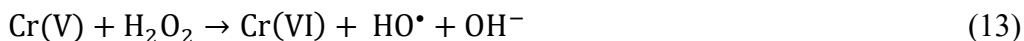
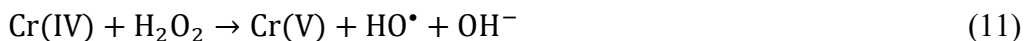
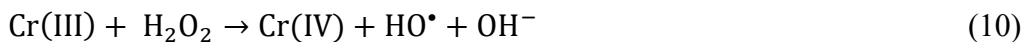


### 1.3. Involvement of Cr(V)/Cr(IV) species in chromium redox reactions of environmental importance

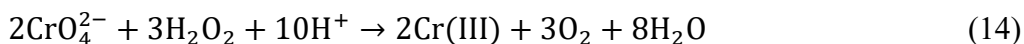
#### 1.3.1. Reactions of Cr(III)/Cr(VI) with hydrogen peroxide

The chemistry between Cr(III) and H<sub>2</sub>O<sub>2</sub> has been extensively studied and reactive intermediates Cr(V) and Cr(IV) are capable of generating HO• from H<sub>2</sub>O<sub>2</sub> by means of Fenton and Haber-Weiss-type reactions.<sup>40-43</sup> The reactions 10-13 illustrate the production of HO• as well as the oxidation of Cr(III).<sup>13</sup> The reaction between Cr(III) and H<sub>2</sub>O<sub>2</sub> gives Cr(IV) and HO• species (reaction 10). The Cr(IV) species may react with H<sub>2</sub>O<sub>2</sub> to form Cr(V) and HO• species (reaction

11). The disproportionation of Cr(IV) may also produce Cr(V) species (reaction 12). The further reaction of Cr(V) with H<sub>2</sub>O<sub>2</sub> may produce Cr(VI) and HO• (reaction 12).



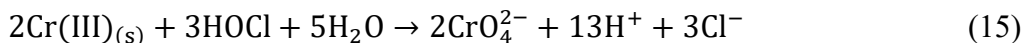
Though Fenton reactions have shown oxidation of organic contaminants utilizing transition metals, they are limiting in that the active metal species is consumed as a reagent and lost through precipitation.<sup>13</sup> This means that metal reagents need to be continuously added to activate H<sub>2</sub>O<sub>2</sub>, resulting in the formation of metal sludge.<sup>13,44</sup> In fact, hydrogen peroxide can function as an oxidant of Cr(III) ( $E^0(\text{H}_2\text{O}_2/\text{H}_2\text{O}) = 1.763\text{V}$ ) and reductant of Cr(VI) ( $E^0(\text{O}_2/\text{H}_2\text{O}_2) = 0.695\text{V}$ ), creating a redox cycle that generates HO• repeatedly.<sup>13,45</sup> The oxidation of Cr(III) by H<sub>2</sub>O<sub>2</sub> can occur at pH > 8.0 and reduction of Cr(VI) (eq. 14<sup>46</sup>) can occur under acidic conditions because the reduction capability of H<sub>2</sub>O<sub>2</sub> increases with decreasing pH.<sup>8,13</sup>



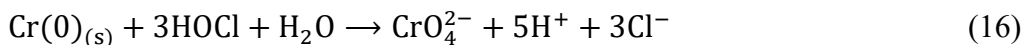
Full reduction of residual Cr(VI) was possible by 1.0 M HCl and 20 mM H<sub>2</sub>O<sub>2</sub>.<sup>46</sup> Subsequently, the use of H<sub>2</sub>O<sub>2</sub> as an advanced oxidation process in chromium-contaminated wastewater to produce HO• and reduce toxic Cr(VI) can be controlled by adjusting the pH of solution. This redox chemistry brings forth evidence showing that utilization of Cr(V)/Cr(IV) species may be feasible in the degradation of pollutants in wastewater.

### 1.3.2. Oxidation of Cr(III) during chlorination

Consequently, Cr(III) can generate Cr(VI) through treating chromium-contaminated water using free chlorine. Characterizing the redox chemistry of chromium in water distribution and treatment is vital for evaluating the potential of Cr(VI) exposure in drinking water. Chlorine used in the disinfection process of drinking water has shown to react with dissolved organic matter and inorganic compounds like bromide ( $\text{Br}^-$ ) forming halogenated disinfection byproducts (DBPs).<sup>47</sup> Not only can DBPs produced by chlorine be highly toxic, but chlorine in water treatment processes has shown to oxidize Cr(III) to Cr(VI) as well.<sup>48-52</sup> Oxidation of Cr(III) by HOCl is highly problematic and trace levels of bromide in this system were shown to be a catalyst in Cr(VI) formation.<sup>50-53</sup> Interestingly, Cr(III) species such as  $\text{Cr}(\text{OH})_3 (s)$  and  $\text{Cr}_2\text{O}_3 (s)$  each revealed different reactivity in chlorine consumption based on their surface area and reactive sites.<sup>51</sup> The oxidation of Cr(III) by HOCl typically proceeds through reaction (15).<sup>52</sup>



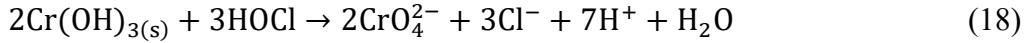
Corrosion of iron pipes in water distribution systems have shown to release chromium, forming mixed phases of Cr(III) – Fe(III) hydroxide that can be oxidized by chlorine.<sup>53</sup> This is of concern to public health because roughly 70% of water distribution pipes in the U.S. are comprised of iron materials and often have a lifespan of multiple decades, giving ample time for chromium to accumulate to high concentrations.<sup>53</sup> Interestingly, Cr(0) that exists in cast iron corrosion scales was shown to be more reactive than Cr(III) with HOCl and the dominant factor of Cr(VI) release in drinking water (reaction 16).<sup>52</sup>



Additionally, the oxidation of  $\text{Br}^-$  by HOCl can produce hypobromous acid (HOBr) which is approximately 6 times faster in oxidizing Cr(III) than HOCl.<sup>51</sup> This indicates that even trace



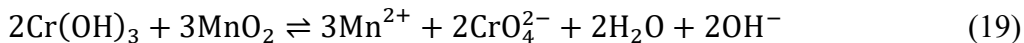
levels of Br<sup>-</sup> should be addressed with caution in solutions where Cr(III) and HOCl are present. The Cr(OH)<sub>3(s)</sub> oxidation rate constants at pH 7.0 and 7.5 are 1.2 x 10<sup>-3</sup> and 1.5 x 10<sup>-3</sup> (M<sup>-1</sup> min<sup>-1</sup>) for HOBr in reactions (reaction 17) and 2.0 x 10<sup>-4</sup> and 2.2 x 10<sup>-4</sup> (M<sup>-1</sup> min<sup>-1</sup>) for HOCl in reaction 18.<sup>51</sup>



### 1.3.3. Oxidation of Cr(III) by solid manganese dioxide

Naturally occurring Cr(III) can be oxidized and lead to Cr(VI) groundwater contamination which has previously caused drinking water concerns.<sup>8</sup> Oxidizing agents of Cr(III) that occur naturally in varying groundwater conditions consist of solid manganese dioxide MnO<sub>x</sub> (Fig. 1.9).<sup>54</sup> The primary oxidizing agent of Cr(III) in alkaline and aerobic conditions are MnO<sub>x</sub> from birnessite mineral; this is due to their large surface areas, degree of crystallinity, strong electronegativity, and ability to regenerate MnO<sub>x</sub> by oxidation of Mn(II) from microorganisms and/or dissolved oxygen.<sup>8,54-56</sup> Oxidation of Mn(II) yielding Mn(III)/(IV) oxides at alkaline and oxic conditions was shown to accelerate Cr(VI) production; this was the dominant pathway of Cr(III) oxidation in long-term analysis (1 year) compared to oxidation by MnO<sub>2</sub> or O<sub>2</sub> (Fig. 1.9).<sup>54,57</sup> The accumulation of MnO<sub>x</sub> in groundwater tables and subsequent oxidation of Cr(III) to Cr(VI) has occurred across the globe, creating drinking water health risks, especially in systems without adequate Cr treatment.<sup>58-</sup>

<sup>60</sup> The following reaction (19) indicates the oxidation of Cr(III) by MnO<sub>x</sub> species:<sup>61</sup>



#### 1.3.4. Reduction of Cr(VI) by natural reducing agents

As for the natural reduction of Cr(VI), reducing agents such as organic matter, Fe(II), and sulfides can reduce Cr(VI) to Cr(III) (Fig. 1.9).<sup>8,54,62,63</sup> Not only is Fe(II) an environmentally-friendly reducing agent, but its application on adsorbed surfaces has shown promising removal of Cr(VI) through consecutive one-electron reduction processes ( $\text{Cr(VI)} + \text{Fe(II)} \rightarrow \text{Cr(V)}$ ;  $\text{Cr(V)} + \text{Fe(II)} \rightarrow \text{Cr(IV)}$ ;  $\text{Cr(IV)} + \text{Fe(II)} \rightarrow \text{Cr(III)}$ ).<sup>64-66</sup> Surface adsorbed Fe(II) is regarded as having higher reducing capabilities than Fe(II) in water, which has been demonstrated in Fe(II)-treated graphene oxide adsorption and reduction of Cr(VI).<sup>67</sup> Clay minerals containing Fe(II)/(III) are capable of reducing Cr(VI), with Fe-poor montmorillonite and Fe-rich nontronite clay minerals having second-order rate constants at pH 7.3 of  $1.28 \text{ M}^{-1}\text{min}^{-1}$  and  $449 \text{ M}^{-1}\text{min}^{-1}$ , respectively.<sup>68</sup> Additionally, some organic ligands can enhance Cr(VI) reduction by Fe(II) from the formation of Fe(II)/(III)-ligand and Cr(V)-ligand complexes.<sup>69</sup> Another example is the reduction of Cr(VI) by biological Fe(II)-complexes (e.g. heme proteins) may result in Cr(V) complexes.<sup>70</sup>

Another effective method in Cr(VI) reduction utilizing Fe(II) has been shown by Fe(II)-doped  $\text{TiO}_2$  photocatalysts; in 3.0 h of sunlight irradiation, almost 100 % of 102.3 mg/L Cr(VI) from plating wastewater was removed.<sup>71</sup> Methods without Fe(II) adsorbed on surfaces, like the Fe(II)/ $\text{H}_2\text{O}_2$  Fenton reaction, has also shown potential to reduce Cr(VI). More recently, incorporating the catalyst  $\text{WS}_2$  was shown to enhance the oxidation of phenol and reduction of Cr(VI), achieving 90.9 % reduction of 40 mg/L Cr(VI) at pH 3.8.<sup>72</sup> These studies that explored incorporating the natural reductant Fe(II) in Cr(VI) reduction yield promising data for its application in Cr-contaminated wastewater. The mechanistic studies involving Cr(V)/Cr(IV) in these systems are lacking.

The reduction of Cr(VI) to Cr(III) can also occur by microorganisms in both aerobic and anaerobic environments.<sup>73</sup> Microorganisms can directly reduce Cr(VI) by intracellular reduction and indirectly reduce Cr(VI) by producing natural reductants.<sup>73</sup> Reductants of Cr(VI) like S(II) and Fe(II) can be produced by bacteria while oxalic acid can be produced by fungi.<sup>8,74</sup> Natural reduction of Cr(VI) has been shown by some fungal species through enzymatic reduction and sorption to mycelia.<sup>62,74</sup> The Cr-resistant fungus *Paecilomyces lilacinus* was shown to reduce 1.24 mg/L of Cr(VI) from tannery effluent to below detection level in 18 hours at both acidic and basic conditions.<sup>75</sup> Additionally, the Cr-tolerant fungus *Penicillium oxalicum* SL2 was shown to reduce 40.6 and 96.1 mg/L of Cr(VI) in 48 and 96 hours, respectively, from electroplating wastewater; a remarkable 89.6 % of 217.1 mg/L Cr(VI) was also reduced from electroplating wastewater in 96 hours.<sup>76</sup> Reduction of Cr(VI) by *Penicillium oxalicum* SL2 was attributed indirectly by oxalic acid production and directly by biomass uptake through amine, carboxyl, and phosphate functional groups.<sup>74</sup> Interestingly, Mn<sup>2+</sup> has shown to promote Cr(VI) reduction by oxalic acid, posing another mechanism for natural Cr(VI) reduction and application to wastewater remediation.<sup>77</sup>

Remediation of chromium-contaminated systems by bacteria has shown to be largely influenced by the bacterial cell surface; gram-negative bacteria are more efficient at reducing Cr(VI) than gram-positive bacteria because their outer membranes contain lipopolysaccharides, lipoproteins, and phospholipids.<sup>78</sup> Furthermore, multiple other microorganisms have shown promising reduction of Cr(VI) making bioremediation of Cr-contaminated environments a viable treatment technology, partly because it can be highly selective to toxic metals.<sup>79</sup> The reduction of Cr(VI) would most likely occur through intermediates, Cr(V) and Cr(IV), which warrants in-depth investigations.

### *1.3.5. Interaction of Cr(VI) with natural organic matter*

Natural organic matter (NOM) contains different components like polysaccharides, proteins, polyphenols, and humic substances (HSs). HSs are produced from microbial and abiotic degradation of different plants and animal wastes. HSs are generally found in river, surface water, soil, groundwater, and sediments. The typical levels of HSs are in the ranges of sub mg/L to mg/L.<sup>80-84</sup> NOM contains many organic compounds with different functional groups such as thiols, carbohydrates, carbonyls, and carboxylic acid.<sup>85-89</sup> Researchers have sub-classified HSs into fulvic acids (FA), humic acids (HA), and humin. FA are considered soluble components over a broad pH range and have low molecular weight constituents. Comparatively, HA are insoluble at low pH and encompass high molecular weight constituents that are usually insoluble at low pH.<sup>90</sup> The insoluble portion at any pH of water is the humin of HS. The procedures to isolate FA, HA, and humin from the sample of HSs have been explained by the International Humic Substance Society. (<https://humic-substances.org/isolation-of-ihss-samples/>)

Many studies have been carried out on the interactions of Cr(VI) with NOM.<sup>91,92</sup> In an earlier work, it was shown that the reduction rate of Cr(VI) with soil FA decreased with the increase in pH.<sup>93,94</sup> The empirical rates from the experimental data indicated that different functional groups of FA reduced Cr(VI). Another study using EPR measurements showed the formation of Cr(V) from the reduction of Cr(VI) by FA (see Fig. 1.10).<sup>95</sup> Model compounds of FA like 1,2-dihydroxybenzene also reduced Cr(VI) to Cr(V) species. Reduction of Cr(VI) is highly dependent on the ionic strength, co-existing ions, and source of NOM.<sup>91,96</sup> Investigations of carboxylic acids (e.g., e.g., formic acid, malic, and malonic), model compounds of HA have been examined for their capacity to reduce Cr(VI). Formation of reactive Cr(V) and Cr(IV) complexes in the Cr(VI)-carboxylic acid interaction have been explored.<sup>97</sup> Literature has clearly suggested

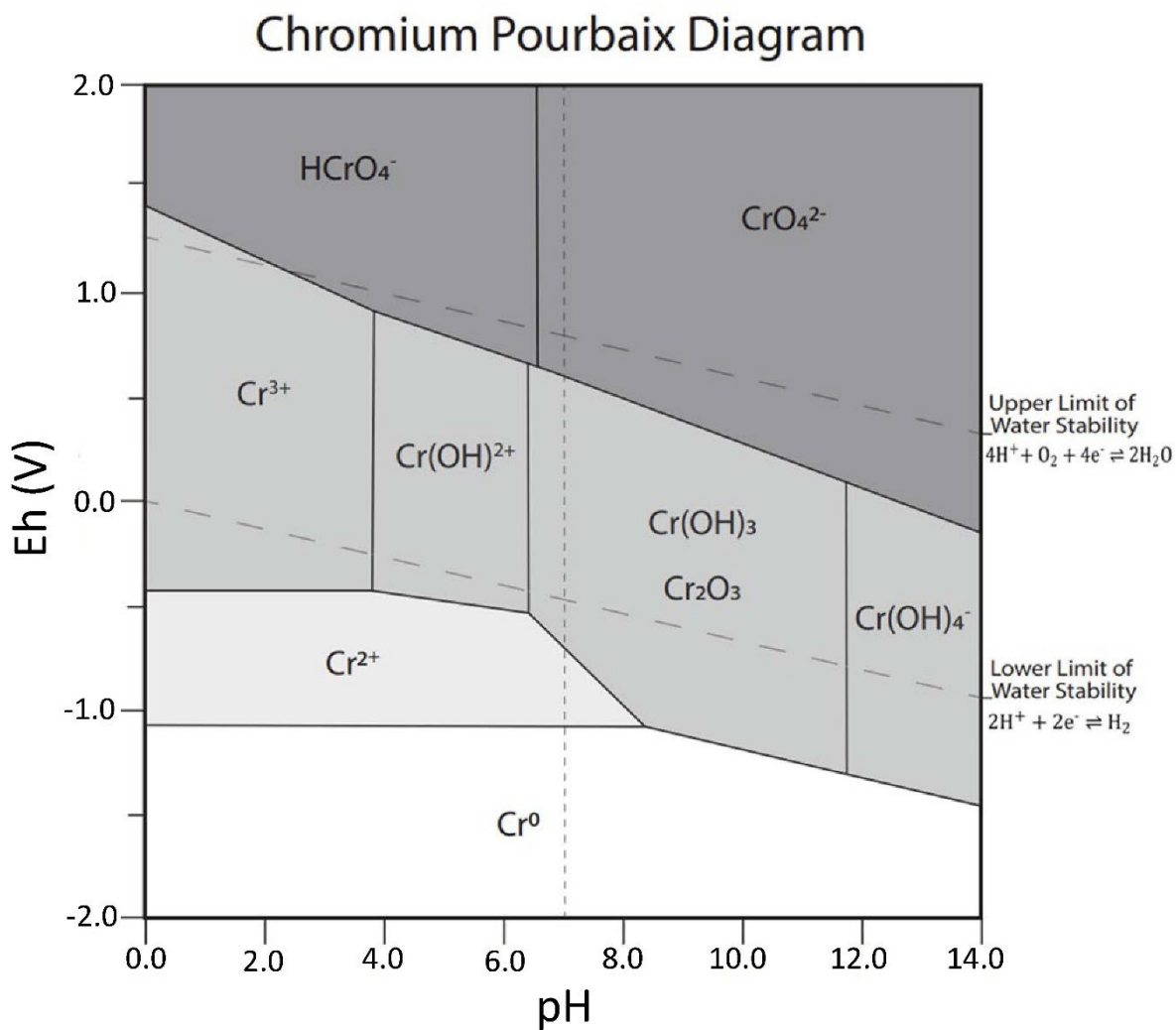
the formation of Cr(V) and Cr(IV) complex species with functional groups of NOM like carbohydrates, carboxylates, hydroxamate, peptides, and proteins. Importantly, the formation of the reactive Cr(V) and Cr(IV) in the Cr(VI)-NOM system may react with co-organic contaminants present in the aquatic environment to cause their degradation.

#### **1.4 Objectives**

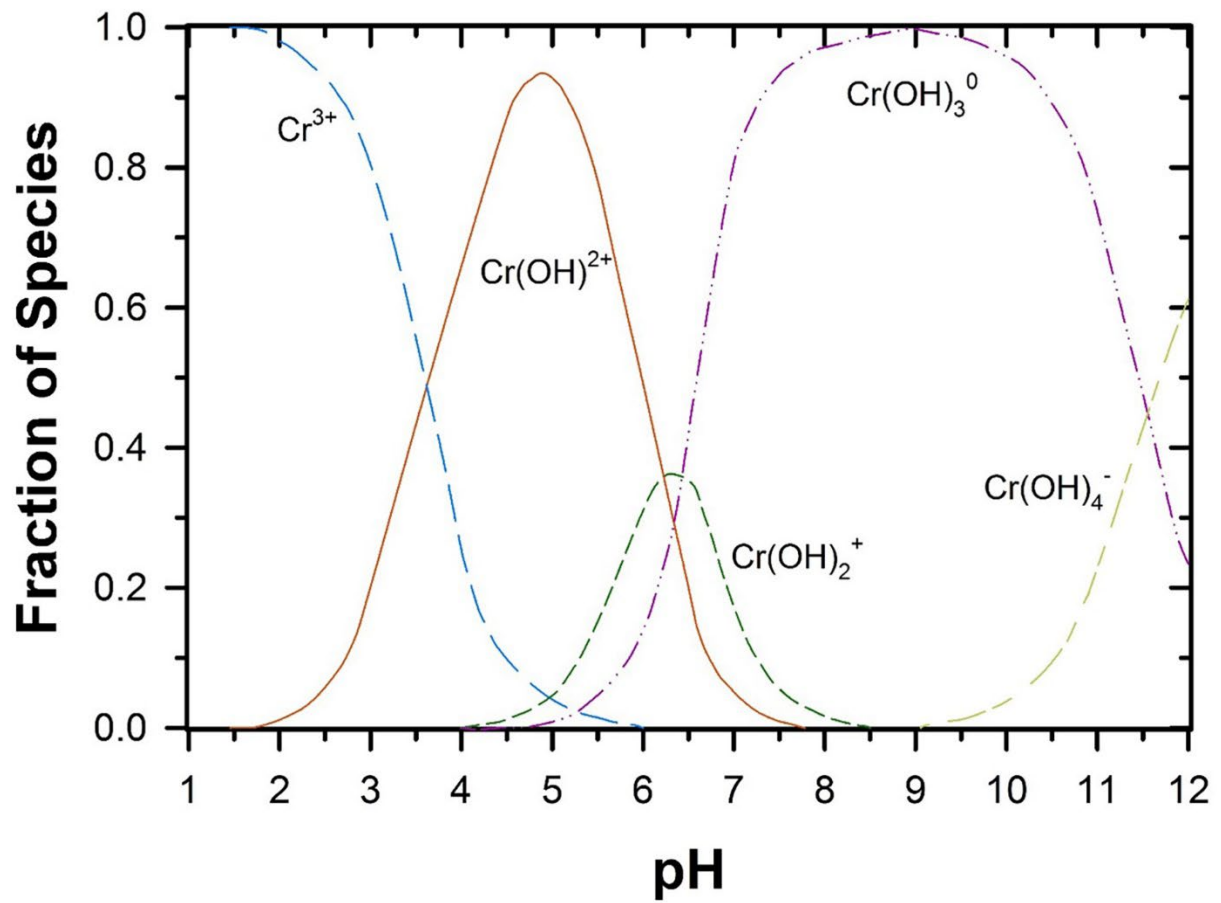
In recent years, peroxyacetic acid ( $\text{CH}_3\text{C}(\text{O})\text{OOH}$ , PAA) has been proposed as an oxidant to remediate organic pollutants in water. Studies are forthcoming on the use of iron(II) and cobalt(III) to activate PAA to enhance the oxidation of organic pollutants in water. In this thesis, the interaction of Cr(III) with PAA was explored with the following aims:

- (i) Study the kinetics of the interaction between PAA and Cr(III) under different environmental pH.
- (ii) Investigate the effect of the interaction of PAA with Cr(III) on the coexisting organic pollutants in water.
- (iii) Determine if different organic pollutants interact differently in the PAA-Cr(III) system.
- (iv) Learn the formation of different reactive species such as reactive oxygen species and high-valent intermediates, Cr(IV) and Cr(V), and Cr(VI) in the PAA-Cr(III) system with and without organic pollutants in water.

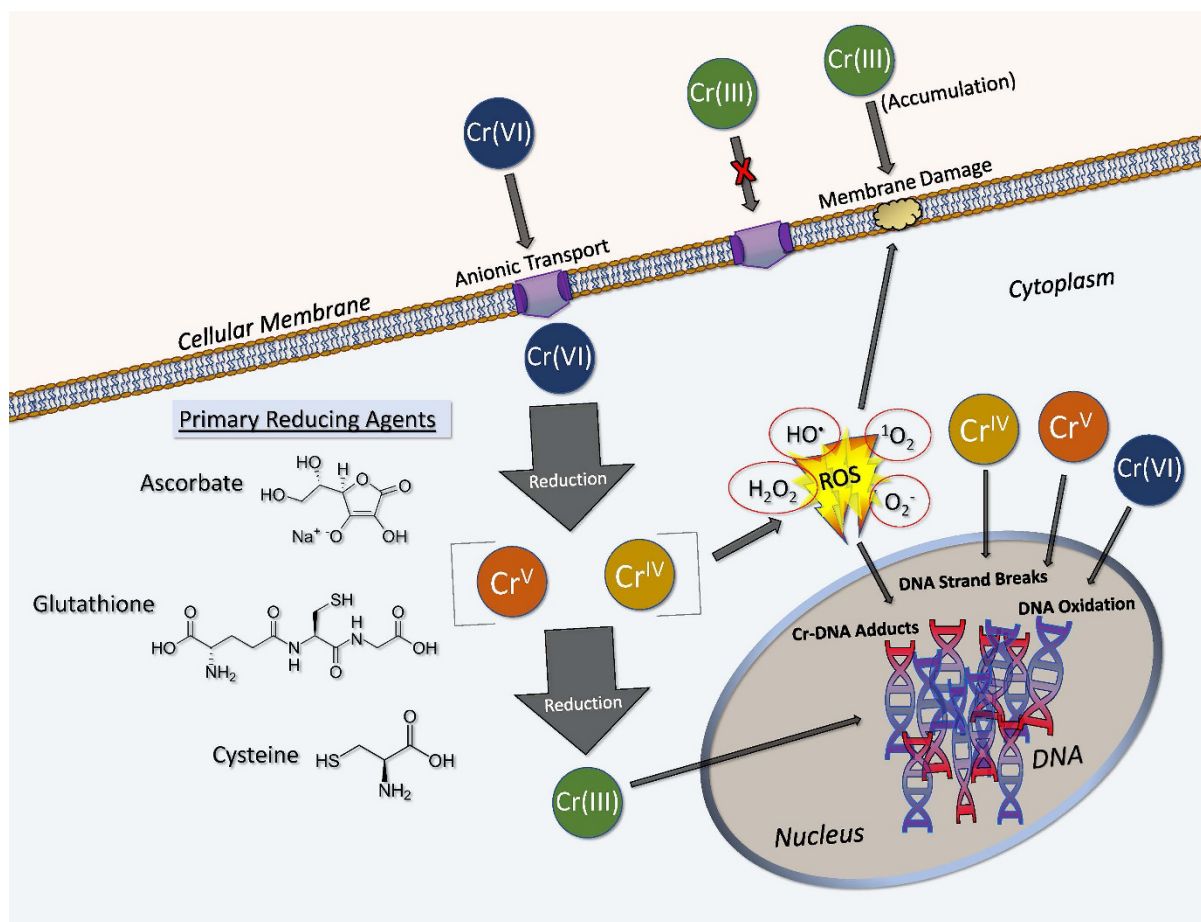
## 1.5. List of Figures



**Fig. 1.1.** Chromium Pourbaix diagram of  $1 \times 10^{-8}$  m total aqueous Cr at  $25^\circ\text{C}$  with darkest to lightest shades indicating oxidation states +6 to 0, respectively; redrawn from <sup>11</sup>.

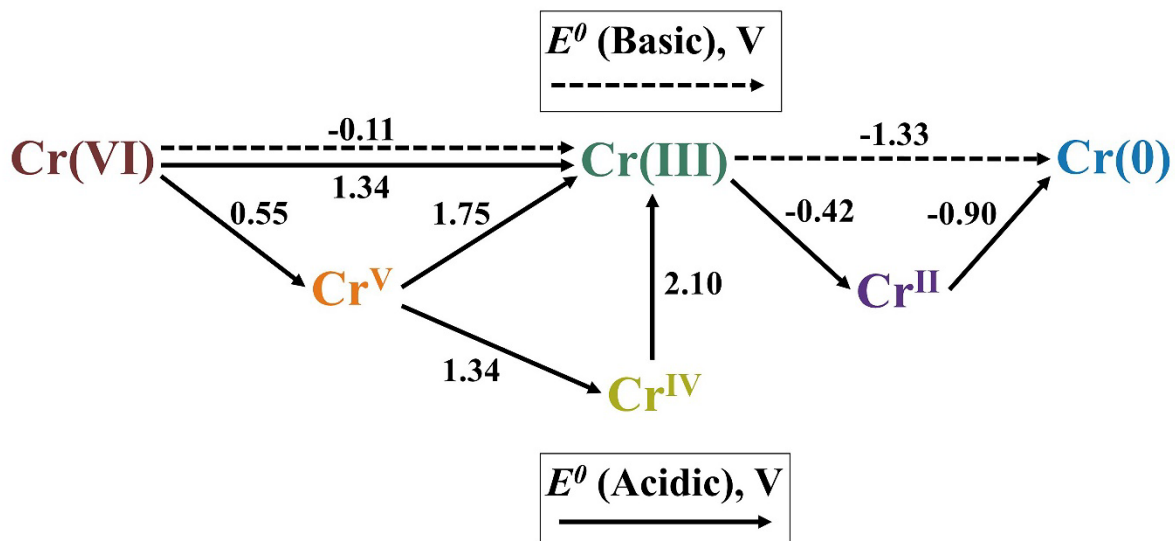


**Fig. 1.2.** Fraction of Cr(III) species as a function of pH with solution in equilibrium with  $\text{Cr(OH)}_3$  (s); redrawn from <sup>12</sup>.

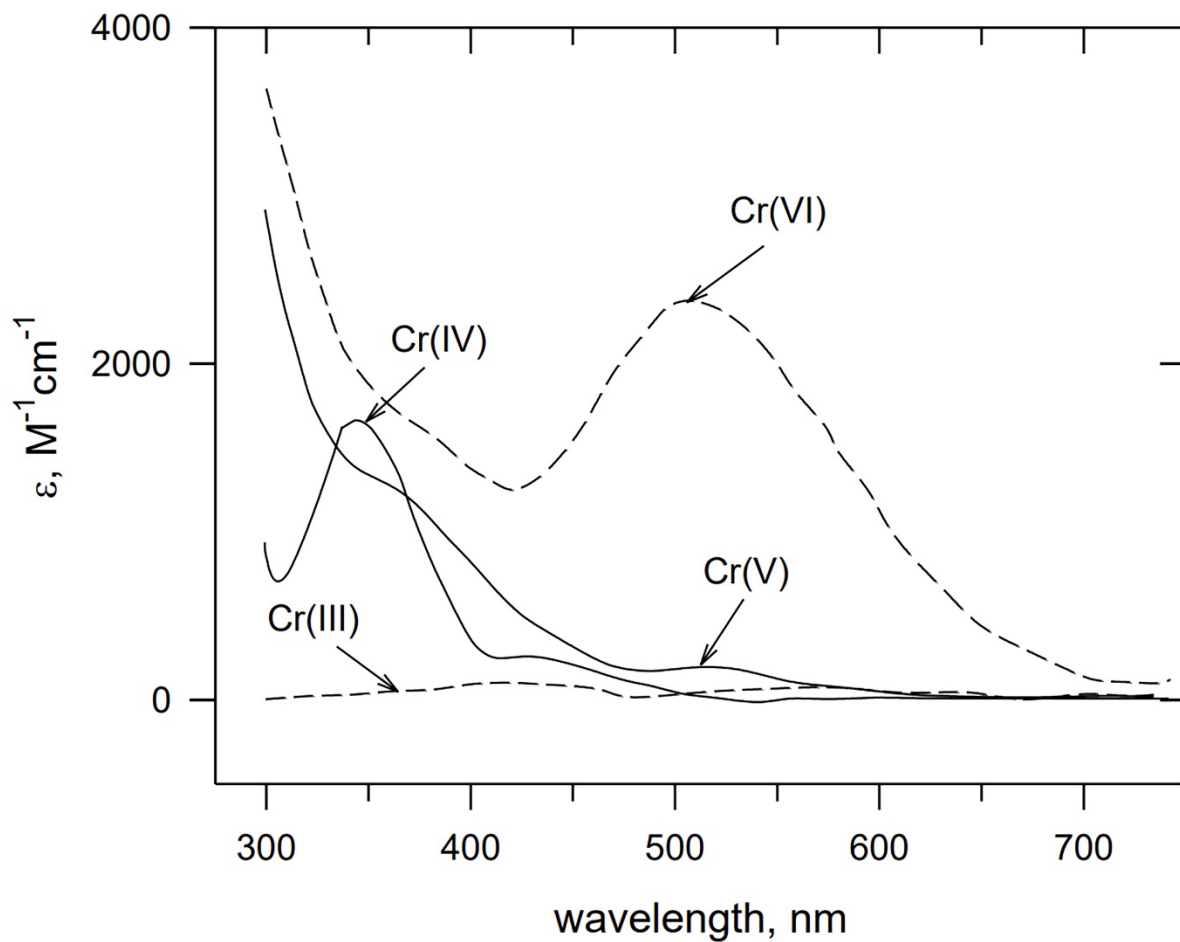


**Fig. 1.3.** Brief overview of chromium cellular entry and subsequent intercellular reduction of  $\text{Cr(VI)}$  which illustrates the role of intermediate  $\text{Cr(IV)}$  and  $\text{Cr(V)}$  in causing DNA damage.

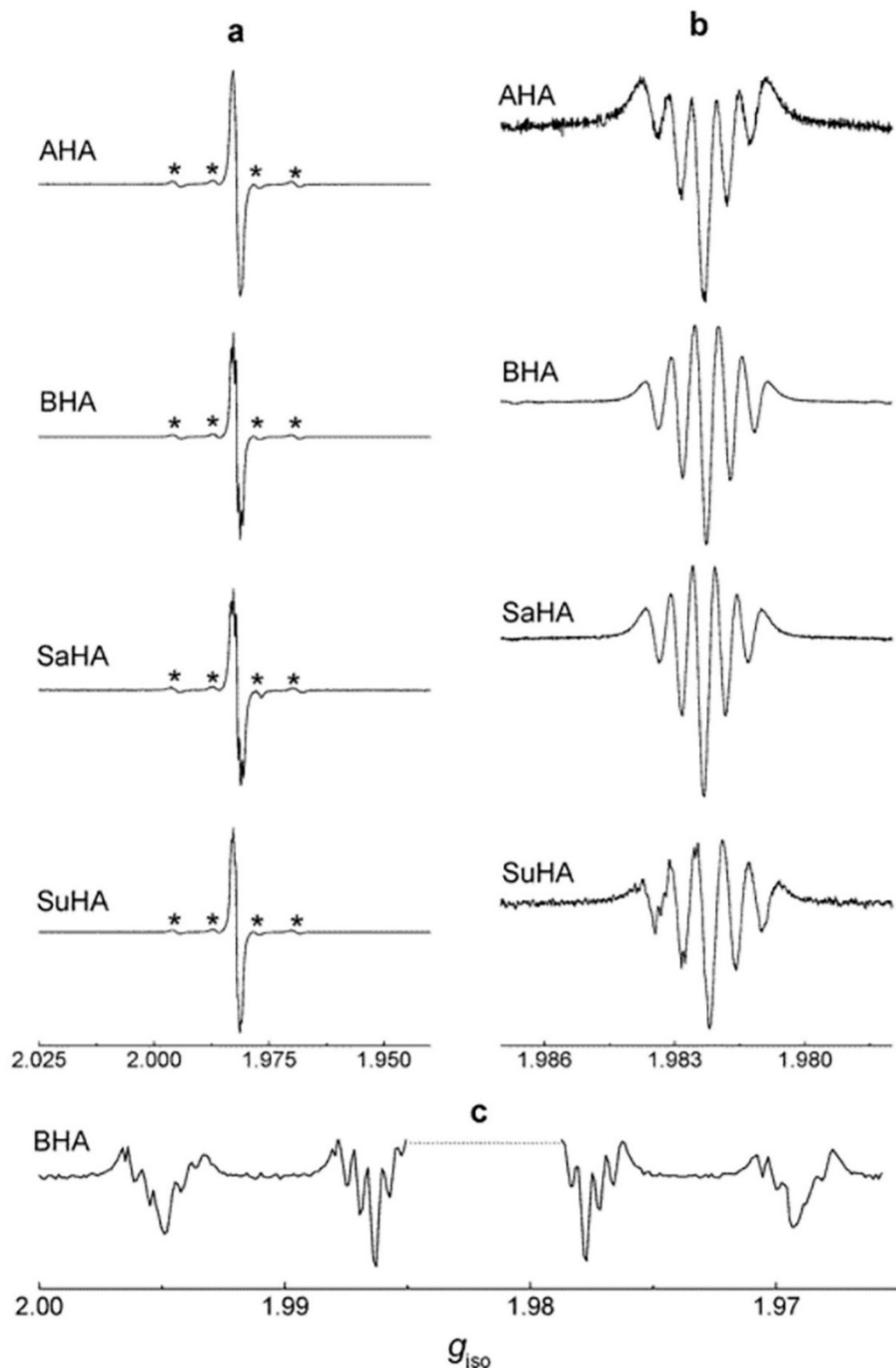




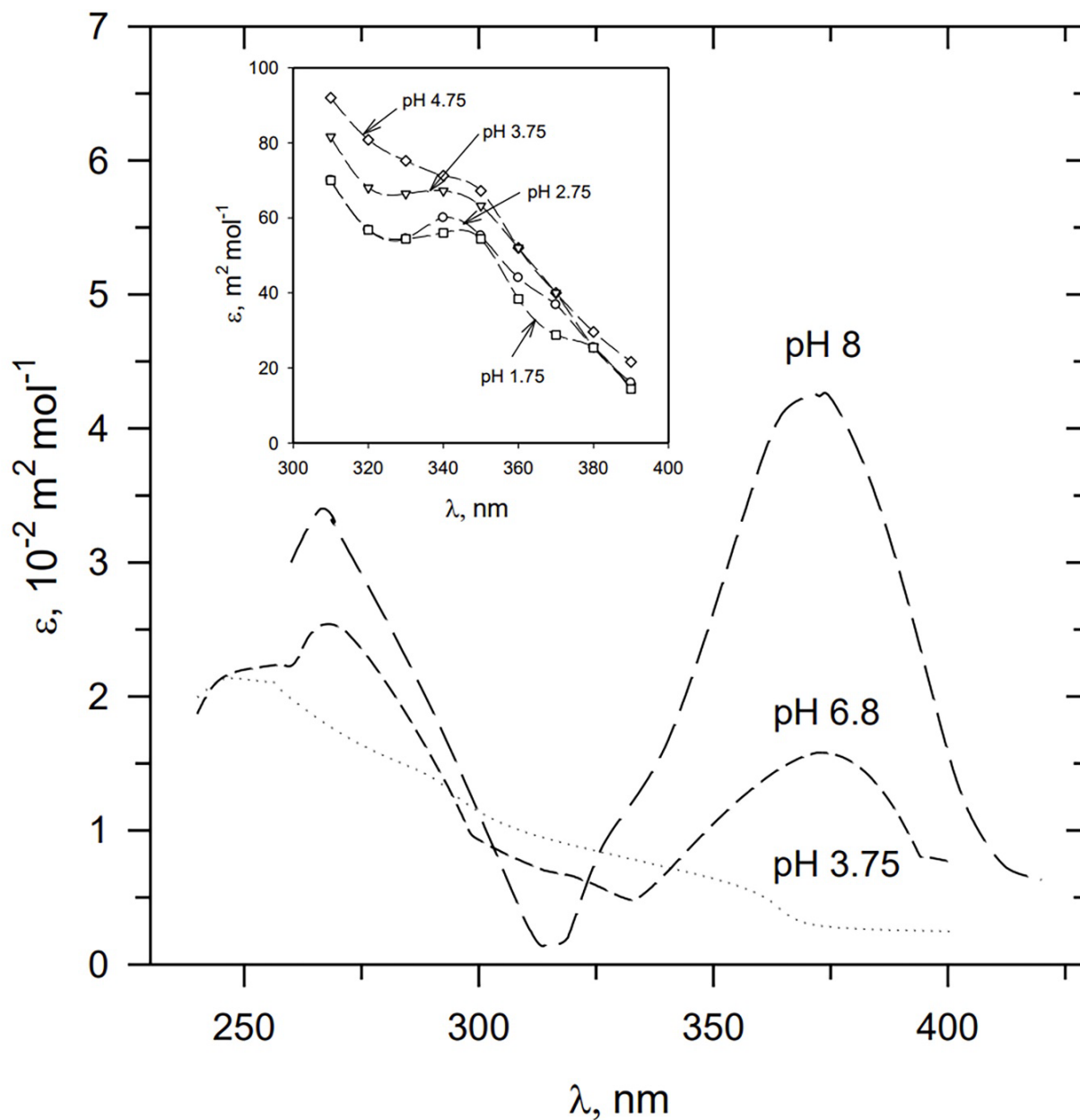
**Fig. 1.4.** Redox potentials ( $E^0$ ) of various Cr species in basic and acidic conditions (reduction potential were taken from <sup>14,34</sup>).



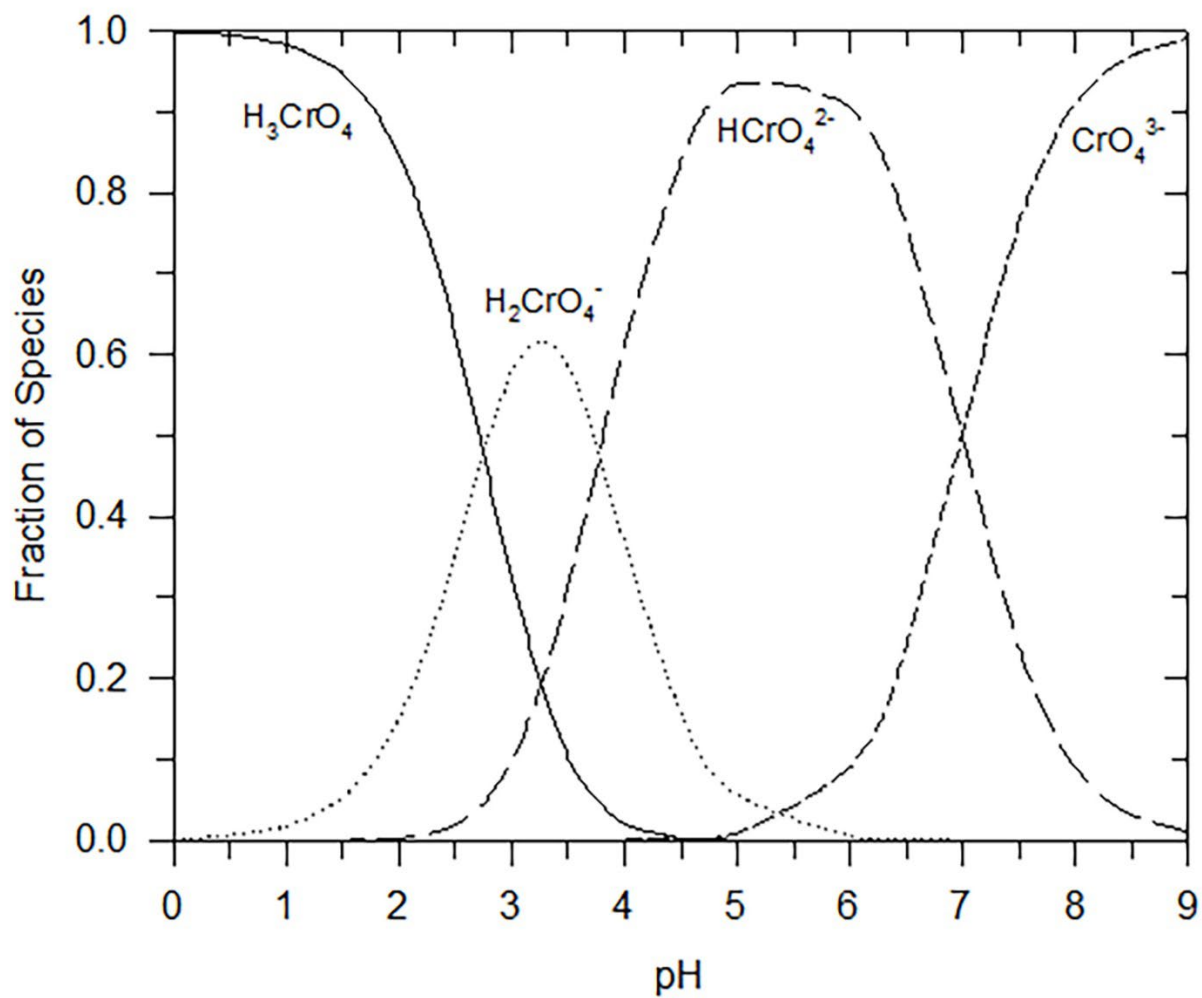
**Fig. 1.5.** The UV-visible spectra of Cr – ehba buffer complex (ehba = 2-ethyl-2-hydroxobutanoato) at pH 3.5 showing varying Cr oxidation states; the Cr(V) complex was  $[CrO(ehba)_2]^-$  and Cr(IV) complex was  $[CrO(ehbaH)_2]^0$ . (Adapted from <sup>14</sup> with permission from John Wiley & Sons, Inc. Copyright 2013).



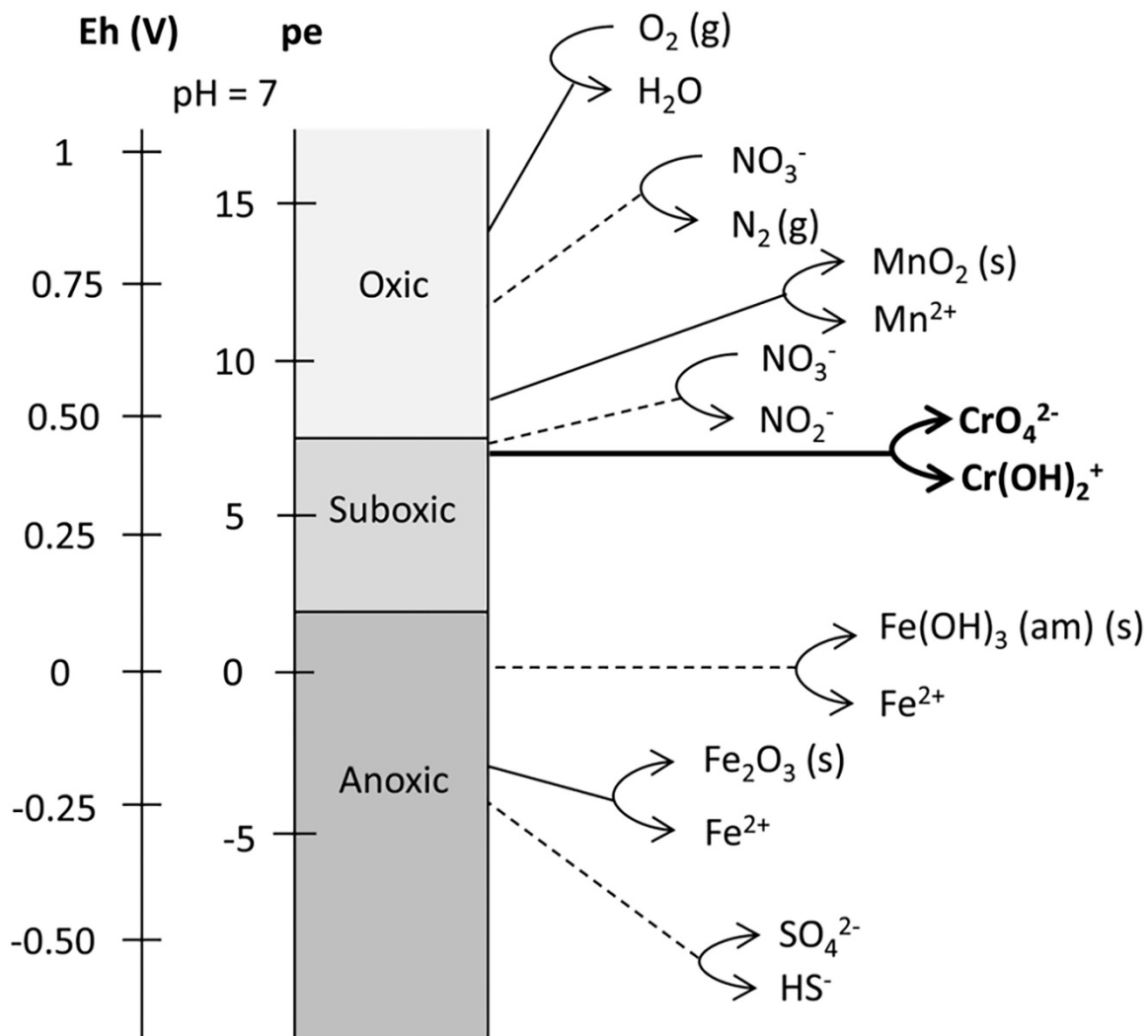
**Fig. 1.6.** Electron Paramagnetic Response (EPR) spectra (X-band) of solutions obtained from reaction between 10 mM Cr(VI) and 0.10 M hydroxamic acids (aceto hydroxamic acid (AHA), benzohydroxamic acid (BHA), salicylhydroxamic acid (SaHA), and subero hydroxamic acid (SuHA)) in *N,N*-dimethylformamide (DMF) for 3.5 hours at 22 °C: (a) first derivative spectra with modulation amplitude at 1.0 G and asterisks indicating satellite signals from  $^{53}\text{Cr}$  hyperfine coupling; (b) second derivative spectra showing only central signals with modulation amplitude at 0.40 G; and (c) second derivative spectra with modulation amplitude at 1.0 G of satellite signals of Cr(V)-BHA complex. (Adapted from <sup>35</sup> with permission from Copyright 2005 American Chemical Society).



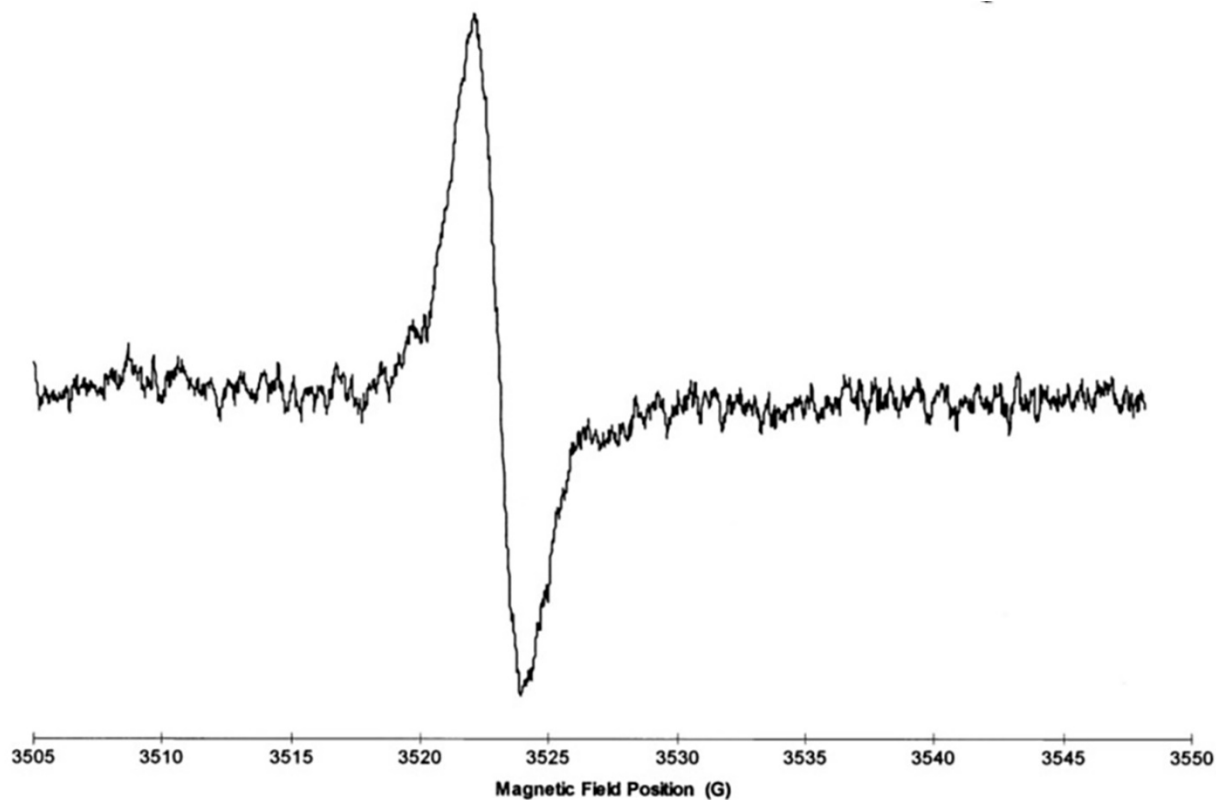
**Fig. 1.7.** The UV-visible spectra of Cr(V) over varying pH obtained by pulse radiolysis from the reaction of Cr(VI) and formate in a  $\text{N}_2\text{O}$  saturated solution; the insert illustrates little variance in Cr(V) spectra in acidic conditions from pH 1.75 to 4.75. (Adapted from <sup>14</sup> with permission from John Wiley & Sons, Inc. Copyright 2013).



**Fig. 1.8.** Speciation of Cr(V) as a function of pH in dilute aqueous solution. (Adapted from <sup>14</sup> with permission from John Wiley & Sons, Inc. Copyright 2013).



**Fig. 1.9.** An environmentally relevant redox potential diagram illustrating the primary redox couples that are thermodynamically capable of influencing Cr redox species. (Adapted from <sup>54</sup> with permission from Elsevier Inc., Copyright 2016).



**Fig. 1.10.** Electron paramagnetic resonance (EPR) spectra of Cr(V) produced from aqueous reaction of equal volumes of 0.14 % (w/v) fulvic-L and 0.020 M  $\text{K}_2\text{Cr(VI)O}_4$  at pH 4.2; EPR conditions were microwave power at 126 mW, receiver gain at  $3.20 \times 10^5$ , and modulation amplitude at 1.6 G. (Adapted from <sup>95</sup> with the permission of Elsevier Inc. Copyright 1998).

## 1.6. References

- (1) Uddin, M. K. A Review on the Adsorption of Heavy Metals by Clay Minerals, with Special Focus on the Past Decade. *Chemical Engineering Journal* **2017**, *308*, 438–462. <https://doi.org/10.1016/j.cej.2016.09.029>.
- (2) Yesil, H.; Molaey, R.; Calli, B.; Tugtas, A. E. Removal and Recovery of Heavy Metals from Sewage Sludge via Three-Stage Integrated Process. *Chemosphere* **2021**, *280*, 130650.
- (3) Shang, H.; Zhang, S.; Zhu, X. Biomass Cellulose Component and Fe Mineral Catalysis Help Cr(VI) to Realize Almost 100% Pyrolysis Reduction Efficiency. *ACS EST Eng.* **2021**, *1* (10), 1441–1448. <https://doi.org/10.1021/acsestengg.1c00174>.
- (4) Zhou, S.; Wei, W.; Chen, L.; Zhang, Z.; Liu, Z.; Wang, Y.; Kong, J.; Li, J. Impact of a Coal-Fired Power Plant Shutdown Campaign on Heavy Metal Emissions in China. *Environ. Sci. Technol.* **2019**, *53* (23), 14063–14069. <https://doi.org/10.1021/acs.est.9b04683>.
- (5) Xu, L.; Zhang, J.; Barnie, S.; Zhang, H.; Liu, F.; Chen, H. New Insight into the Adsorption Mechanism of PCP by Humic Substances with Different Degrees of Humification in the Presence of Cr (VI). *Chemosphere* **2021**, 131223.
- (6) Choppala, G.; Bolan, N.; Park, J. H. Chapter Two - Chromium Contamination and Its Risk Management in Complex Environmental Settings. In *Advances in Agronomy*; Sparks, D. L., Ed.; Academic Press, 2013; Vol. 120, pp 129–172. <https://doi.org/10.1016/B978-0-12-407686-0.00002-6>.
- (7) Deng, Y.; Wang, M.; Tian, T.; Lin, S.; Xu, P.; Zhou, L.; Dai, C.; Hao, Q.; Wu, Y.; Zhai, Z.; Zhu, Y.; Zhuang, G.; Dai, Z. The Effect of Hexavalent Chromium on the Incidence and



- Mortality of Human Cancers: A Meta-Analysis Based on Published Epidemiological Cohort Studies. *Front. Oncol.* **2019**, *9*, 24. <https://doi.org/10.3389/fonc.2019.00024>.
- (8) Liang, J.; Huang, X.; Yan, J.; Li, Y.; Zhao, Z.; Liu, Y.; Ye, J.; Wei, Y. A Review of the Formation of Cr(VI) via Cr(III) Oxidation in Soils and Groundwater. *Science of The Total Environment* **2021**, *774*, 145762. <https://doi.org/10.1016/j.scitotenv.2021.145762>.
- (9) Das, P. K.; Das, B. P.; Dash, P. Chromite Mining Pollution, Environmental Impact, Toxicity and Phytoremediation: A Review. *Environ Chem Lett* **2020**. <https://doi.org/10.1007/s10311-020-01102-w>.
- (10) *Encyclopedia of Geochemistry: A Comprehensive Reference Source on the Chemistry of the Earth*; White, W. M., Ed.; Encyclopedia of Earth Sciences Series; Springer International Publishing: Cham, 2018. <https://doi.org/10.1007/978-3-319-39312-4>.
- (11) Beverskog, B.; Puigdomenech, I. Revised Pourbaix Diagrams for Chromium at 25–300 °C. *Corrosion Science* **1997**, *39* (1), 43–57. [https://doi.org/10.1016/S0010-938X\(97\)89244-X](https://doi.org/10.1016/S0010-938X(97)89244-X).
- (12) Richard, F. C.; Bourg, A. C. M. Aqueous Geochemistry of Chromium: A Review. *Water Research* **1991**, *25* (7), 807–816. [https://doi.org/10.1016/0043-1354\(91\)90160-R](https://doi.org/10.1016/0043-1354(91)90160-R).
- (13) Bokare, A. D.; Choi, W. Advanced Oxidation Process Based on the Cr(III)/Cr(VI) Redox Cycle. *Environ. Sci. Technol.* **2011**, *45* (21), 9332–9338. <https://doi.org/10.1021/es2021704>.
- (14) Sharma, V. K. High-Valent Cr, Mn, and Fe Species. In *Oxidation of Amino Acids, Peptides, and Proteins*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2012; pp 278–382. <https://doi.org/10.1002/9781118482469.ch6>.

- (15) Lindqvist-Reis, P.; Muñoz-Páez, A.; Díaz-Moreno, S.; Pattanaik, S.; Persson, I.; Sandström, M. The Structure of the Hydrated Gallium(III), Indium(III), and Chromium(III) Ions in Aqueous Solution. A Large Angle X-Ray Scattering and EXAFS Study. *Inorg. Chem.* **1998**, *37* (26), 6675–6683. <https://doi.org/10.1021/ic980750y>.
- (16) DesMarias, T. L.; Costa, M. Mechanisms of Chromium-Induced Toxicity. *Current Opinion in Toxicology* **2019**, *14*, 1–7. <https://doi.org/10.1016/j.cotox.2019.05.003>.
- (17) Unceta, N.; Astorkia, M.; Abrego, Z.; Gómez-Caballero, A.; Goicolea, M. A.; Barrio, R. J. A Novel Strategy for Cr(III) and Cr(VI) Analysis in Dietary Supplements by Speciated Isotope Dilution Mass Spectrometry. *Talanta* **2016**, *154*, 255–262. <https://doi.org/10.1016/j.talanta.2016.03.079>.
- (18) Stearns, D. M.; Wise, J. P.; Patierno, S. R.; Wetterhahn, K. E. Chromium(III) Picolinate Produces Chromosome Damage in Chinese Hamster Ovary Cells. *The FASEB Journal* **1995**, *9* (15), 1643–1648. <https://doi.org/10.1096/fasebj.9.15.8529845>.
- (19) Andersson, M. A.; Petersson Grawé, K. V.; Karlsson, O. M.; Abramsson-Zetterberg, L. A. G.; Hellman, B. E. Evaluation of the Potential Genotoxicity of Chromium Picolinate in Mammalian Cells in Vivo and in Vitro. *Food and Chemical Toxicology* **2007**, *45* (7), 1097–1106. <https://doi.org/10.1016/j.fct.2006.11.008>.
- (20) Stout, M. D.; Nyska, A.; Collins, B. J.; Witt, K. L.; Kissling, G. E.; Malarkey, D. E.; Hooth, M. J. Chronic Toxicity and Carcinogenicity Studies of Chromium Picolinate Monohydrate Administered in Feed to F344/N Rats and B6C3F1 Mice for 2 Years. *Food and Chemical Toxicology* **2009**, *47* (4), 729–733. <https://doi.org/10.1016/j.fct.2009.01.006>.

- (21) Costa, M.; Klein, C. B. Toxicity and Carcinogenicity of Chromium Compounds in Humans. *Critical Reviews in Toxicology* **2006**, *36* (2), 155–163.  
<https://doi.org/10.1080/10408440500534032>.
- (22) Hausladen, D. M.; Alexander-Ozinskas, A.; McClain, C.; Fendorf, S. Hexavalent Chromium Sources and Distribution in California Groundwater. *Environ. Sci. Technol.* **2018**, *52* (15), 8242–8251. <https://doi.org/10.1021/acs.est.7b06627>.
- (23) Levina, A.; Zhang, L.; Lay, P. A. Formation and Reactivity of Chromium(V)–Thiolato Complexes: A Model for the Intracellular Reactions of Carcinogenic Chromium(VI) with Biological Thiols. *J. Am. Chem. Soc.* **2010**, *132* (25), 8720–8731.  
<https://doi.org/10.1021/ja101675w>.
- (24) Headlam, H. A.; Lay, P. A. Spectroscopic Characterization of Genotoxic Chromium(V) Peptide Complexes: Oxidation of Chromium(III) Triglycine, Tetraglycine and Pentaglycine Complexes. *Journal of Inorganic Biochemistry* **2016**, *162*, 227–237.  
<https://doi.org/10.1016/j.jinorgbio.2016.06.015>.
- (25) Wani, P. A.; Wani, J. A.; Wahid, S. Recent Advances in the Mechanism of Detoxification of Genotoxic and Cytotoxic Cr (VI) by Microbes. *Journal of Environmental Chemical Engineering* **2018**, *6* (4), 3798–3807. <https://doi.org/10.1016/j.jece.2018.05.042>.
- (26) Wang, Y.; Su, H.; Gu, Y.; Song, X.; Zhao, J. Carcinogenicity of Chromium and Chemoprevention: A Brief Update. *OTT* **2017**, *Volume 10*, 4065–4079.  
<https://doi.org/10.2147/OTT.S139262>.
- (27) Brauer, S. L.; Hneihen, A. S.; McBride, J. S.; Wetterhahn, K. E. Chromium(VI) Forms Thiolate Complexes with  $\gamma$ -Glutamylcysteine, *N*-Acetylcysteine, Cysteine, and the

- Methyl Ester of *N*-Acetylcysteine. *Inorg. Chem.* **1996**, *35* (2), 373–381.  
<https://doi.org/10.1021/ic941452d>.
- (28) Pavesi, T.; Moreira, J. C. Mechanisms and Individuality in Chromium Toxicity in Humans. *J Appl Toxicol* **2020**, *40* (9), 1183–1197. <https://doi.org/10.1002/jat.3965>.
- (29) Wakeman, T. P.; Yang, A.; Dalal, N. S.; Boohaker, R. J.; Zeng, Q.; Ding, Q.; Xu, B. DNA Mismatch Repair Protein Mlh1 Is Required for Tetravalent Chromium Intermediate-Induced DNA Damage. *Oncotarget* **2017**, *8* (48), 83975–83985.  
<https://doi.org/10.18632/oncotarget.20150>.
- (30) Pattison, D. I.; Lay, P. A.; Davies, M. J. EPR Studies of Chromium(V) Intermediates Generated via Reduction of Chromium(VI) by DOPA and Related Catecholamines: Potential Role for Oxidized Amino Acids in Chromium-Induced Cancers. *Inorg. Chem.* **2000**, *39* (13), 2729–2739. <https://doi.org/10.1021/ic991443a>.
- (31) Levina, A.; Zhang, L.; Lay, P. A. Structure and Reactivity of a Chromium(V) Glutathione Complex <sup>1</sup>. *Inorg. Chem.* **2003**, *42* (3), 767–784. <https://doi.org/10.1021/ic020621o>.
- (32) Levina, A.; Harris, H. H.; Lay, P. A. X-Ray Absorption and EPR Spectroscopic Studies of the Biotransformations of Chromium(VI) in Mammalian Cells. Is Chromodulin an Artifact of Isolation Methods? *J. Am. Chem. Soc.* **2007**, *129* (5), 1065–1075.  
<https://doi.org/10.1021/ja063792r>.
- (33) Lay, P. A.; Levina, A. Activation of Molecular Oxygen during the Reactions of Chromium(VI/V/IV) with Biological Reductants: Implications for Chromium-Induced Genotoxicities <sup>1</sup>. *J. Am. Chem. Soc.* **1998**, *120* (27), 6704–6714.  
<https://doi.org/10.1021/ja974240z>.

- (34) Dong, H.; Wei, G.; Cao, T.; Shao, B.; Guan, X.; Strathmann, T. J. Insights into the Oxidation of Organic Cocontaminants during Cr(VI) Reduction by Sulfite: The Overlooked Significance of Cr(V). *Environ. Sci. Technol.* **2020**, *54* (2), 1157–1166. <https://doi.org/10.1021/acs.est.9b03356>.
- (35) Gez, S.; Luxenhofer, R.; Levina, A.; Codd, R.; Lay, P. A. Chromium (V) Complexes of Hydroxamic Acids: Formation, Structures, and Reactivities. *Inorganic chemistry* **2005**, *44* (8), 2934–2943.
- (36) Orłowska, E.; Roller, A.; Wiesinger, H.; Pignitter, M.; Jirsa, F.; Krachler, R.; Kandioller, W.; Keppler, B. K. Benzoic Hydroxamate-Based Iron Complexes as Model Compounds for Humic Substances: Synthesis, Characterization and Algal Growth Experiments. *RSC advances* **2016**, *6* (46), 40238–40249.
- (37) Santos-Carballal, D.; Du, Z.; King, H. E.; De Leeuw, N. H. A Computational Study of the Interaction of Organic Surfactants with Goethite  $\alpha$ -FeO (OH) Surfaces. *RSC advances* **2016**, *6* (94), 91893–91903.
- (38) Codd, R.; Dillon, C. T.; Levina, A.; Lay, P. A. Studies on the Genotoxicity of Chromium: From the Test Tube to the Cell. *Coordination Chemistry Reviews* **2001**, *216–217*, 537–582. [https://doi.org/10.1016/S0010-8545\(00\)00408-2](https://doi.org/10.1016/S0010-8545(00)00408-2).
- (39) Buxton, G. V.; Djouider, F. Disproportionation of Cr V Generated by the Radiation-Induced Reduction of Cr VI in Aqueous Solution Containing Formate: A Pulse Radiolysis Study. *Faraday Trans.* **1996**, *92* (21), 4173. <https://doi.org/10.1039/ft9969204173>.
- (40) Shi, X. REDUCTION OF CHROMIUM (VI) AND ITS RELATIONSHIP TO CARCINOGENESIS. *Journal of Toxicology and Environmental Health, Part B* **1999**, *2* (1), 87–104. <https://doi.org/10.1080/109374099281241>.

- (41) Shi, X.; Mao, Y.; Knapton, A. D.; Ding, M.; Rojanasakul, Y.; Gannett, P. M.; Dalal, N.; Liu, K. Reaction of Cr(VI) with Ascorbate and Hydrogen Peroxide Generates Hydroxyl Radicals and Causes DNA Damage: Role of a Cr(IV)-Mediated Fenton-like Reaction. *Carcinogenesis* **1994**, *15* (11), 2475–2478. <https://doi.org/10.1093/carcin/15.11.2475>.
- (42) Shi, X.; Dalal, N. S. The Role of Superoxide Radical in Chromium(VI)-Generated Hydroxyl Radical: The Cr(VI) Haber-Weiss Cycle. *Archives of Biochemistry and Biophysics* **1992**, *292* (1), 323–327. [https://doi.org/10.1016/0003-9861\(92\)90085-B](https://doi.org/10.1016/0003-9861(92)90085-B).
- (43) Bokare, A. D.; Choi, W. Review of Iron-Free Fenton-like Systems for Activating H<sub>2</sub>O<sub>2</sub> in Advanced Oxidation Processes. *Journal of Hazardous Materials* **2014**, *275*, 121–135. <https://doi.org/10.1016/j.jhazmat.2014.04.054>.
- (44) Xu, M.; Wu, C.; Zhou, Y. Advancements in the Fenton Process for Wastewater Treatment. In *Advanced Oxidation Processes - Applications, Trends, and Prospects*; Bustillo-Lecompte, C., Ed.; IntechOpen, 2020. <https://doi.org/10.5772/intechopen.90256>.
- (45) Armstrong, D. A.; Huie, R. E.; Lyman, S.; Koppenol, W. H.; Merényi, G.; Neta, P.; Stanbury, D. M.; Steenken, S.; Wardman, P. Standard Electrode Potentials Involving Radicals in Aqueous Solution: Inorganic Radicals. *BioInorganic Reaction Mechanisms* **2013**, *9* (1–4). <https://doi.org/10.1515/irm-2013-0005>.
- (46) Bokare, A. D.; Choi, W. Chromate-Induced Activation of Hydrogen Peroxide for Oxidative Degradation of Aqueous Organic Pollutants. *Environ. Sci. Technol.* **2010**, *44* (19), 7232–7237. <https://doi.org/10.1021/es903930h>.
- (47) Allard, S.; Tan, J.; Joll, C. A.; von Gunten, U. Mechanistic Study on the Formation of Cl-/Br-/I-Trihalomethanes during Chlorination/Chloramination Combined with a Theoretical

- Cytotoxicity Evaluation. *Environ. Sci. Technol.* **2015**, *49* (18), 11105–11114.  
<https://doi.org/10.1021/acs.est.5b02624>.
- (48) Yang, Y.; Komaki, Y.; Kimura, S. Y.; Hu, H.-Y.; Wagner, E. D.; Mariñas, B. J.; Plewa, M. J. Toxic Impact of Bromide and Iodide on Drinking Water Disinfected with Chlorine or Chloramines. *Environ. Sci. Technol.* **2014**, *48* (20), 12362–12369.  
<https://doi.org/10.1021/es503621e>.
- (49) Richardson, S. D.; Plewa, M. J.; Wagner, E. D.; Schoeny, R.; DeMarini, D. M. Occurrence, Genotoxicity, and Carcinogenicity of Regulated and Emerging Disinfection by-Products in Drinking Water: A Review and Roadmap for Research. *Mutation Research/Reviews in Mutation Research* **2007**, *636* (1), 178–242.  
<https://doi.org/10.1016/j.mrrev.2007.09.001>.
- (50) Lee, G.; Hering, J. G. Oxidative Dissolution of Chromium(III) Hydroxide at PH 9, 3, and 2 with Product Inhibition at PH 2. *Environ. Sci. Technol.* **2005**, *39* (13), 4921–4928.  
<https://doi.org/10.1021/es048073w>.
- (51) Chebeir, M.; Liu, H. Kinetics and Mechanisms of Cr(VI) Formation via the Oxidation of Cr(III) Solid Phases by Chlorine in Drinking Water. *Environ. Sci. Technol.* **2016**, *50* (2), 701–710. <https://doi.org/10.1021/acs.est.5b05739>.
- (52) Tan, C.; Avasarala, S.; Liu, H. Hexavalent Chromium Release in Drinking Water Distribution Systems: New Insights into Zerovalent Chromium in Iron Corrosion Scales. *Environ. Sci. Technol.* **2020**, *54* (20), 13036–13045.  
<https://doi.org/10.1021/acs.est.0c03922>.

- (53) Chebeir, M.; Liu, H. Oxidation of Cr(III)–Fe(III) Mixed-Phase Hydroxides by Chlorine: Implications on the Control of Hexavalent Chromium in Drinking Water. *Environ. Sci. Technol.* **2018**, *52* (14), 7663–7670. <https://doi.org/10.1021/acs.est.7b06013>.
- (54) Gorny, J.; Billon, G.; Noiriél, C.; Dumoulin, D.; Lesven, L.; Madé, B. Chromium Behavior in Aquatic Environments: A Review. *Environ. Rev.* **2016**, *24* (4), 503–516. <https://doi.org/10.1139/er-2016-0012>.
- (55) Zhitkovich, A. Chromium in Drinking Water: Sources, Metabolism, and Cancer Risks. *Chem. Res. Toxicol.* **2011**, *24* (10), 1617–1629. <https://doi.org/10.1021/tx200251t>.
- (56) Dai, R.; Liu, J.; Yu, C.; Sun, R.; Lan, Y.; Mao, J.-D. A Comparative Study of Oxidation of Cr(III) in Aqueous Ions, Complex Ions and Insoluble Compounds by Manganese-Bearing Mineral (Birnessite). *Chemosphere* **2009**, *76* (4), 536–541. <https://doi.org/10.1016/j.chemosphere.2009.03.009>.
- (57) Liu, W.; Li, J.; Zheng, J.; Song, Y.; Shi, Z.; Lin, Z.; Chai, L. Different Pathways for Cr(III) Oxidation: Implications for Cr(VI) Reoccurrence in Reduced Chromite Ore Processing Residue. *Environ. Sci. Technol.* **2020**, *54* (19), 11971–11979. <https://doi.org/10.1021/acs.est.0c01855>.
- (58) Coyte, R. M.; Vengosh, A. Factors Controlling the Risks of Co-Occurrence of the Redox-Sensitive Elements of Arsenic, Chromium, Vanadium, and Uranium in Groundwater from the Eastern United States. *Environ. Sci. Technol.* **2020**, *54* (7), 4367–4375. <https://doi.org/10.1021/acs.est.9b06471>.
- (59) Guo, H.; Chen, Y.; Hu, H.; Zhao, K.; Li, H.; Yan, S.; Xiu, W.; Coyte, R. M.; Vengosh, A. High Hexavalent Chromium Concentration in Groundwater from a Deep Aquifer in the



- Baiyangdian Basin of the North China Plain. *Environ. Sci. Technol.* **2020**, *54* (16), 10068–10077. <https://doi.org/10.1021/acs.est.0c02357>.
- (60) Kaprara, E.; Kazakis, N.; Simeonidis, K.; Coles, S.; Zouboulis, A. I.; Samaras, P.; Mitrakas, M. Occurrence of Cr(VI) in Drinking Water of Greece and Relation to the Geological Background. *Journal of Hazardous Materials* **2015**, *281*, 2–11. <https://doi.org/10.1016/j.jhazmat.2014.06.084>.
- (61) Kimbrough, D. E.; Cohen, Y.; Winer, A. M.; Creelman, L.; Mabuni, C. A Critical Assessment of Chromium in the Environment. *Critical Reviews in Environmental Science and Technology* **1999**, *29* (1), 1–46. <https://doi.org/10.1080/10643389991259164>.
- (62) Barrera-Díaz, C. E.; Lugo-Lugo, V.; Bilyeu, B. A Review of Chemical, Electrochemical and Biological Methods for Aqueous Cr(VI) Reduction. *Journal of Hazardous Materials* **2012**, *223–224*, 1–12. <https://doi.org/10.1016/j.jhazmat.2012.04.054>.
- (63) Liao, P.; Pan, C.; Ding, W.; Li, W.; Yuan, S.; Fortner, J. D.; Giammar, D. E. Formation and Transport of Cr(III)-NOM-Fe Colloids upon Reaction of Cr(VI) with NOM-Fe(II) Colloids at Anoxic–Oxic Interfaces. *Environ. Sci. Technol.* **2020**, *54* (7), 4256–4266. <https://doi.org/10.1021/acs.est.9b07934>.
- (64) Westheimer, F. H. The Mechanisms of Chromic Acid Oxidations. *Chemical reviews* **1949**, *45* (3), 419–451.
- (65) Yuan, Y.; Wei, X.; Yin, H.; Zhu, M.; Luo, H.; Dang, Z. Synergistic Removal of Cr (VI) by S-NZVI and Organic Acids: The Enhanced Electron Selectivity and PH-Dependent Promotion Mechanism. *Journal of Hazardous Materials* **2021**, 127240.
- (66) Zhang, Y.; Zhu, Z.; Liao, Y.; Dang, Z.; Guo, C. Effects of Fe(II) Source on the Formation and Reduction Rate of Biosynthetic Mackinawite: Biosynthesis Process and Removal of

- Cr(VI). *Chemical Engineering Journal* **2021**, 421, 129723.  
<https://doi.org/10.1016/j.cej.2021.129723>.
- (67) Chen, J.; Wu, H.; Xu, L.; Li, M.; Du, K.; Sheng, G. New Insights into Colloidal GO, Cr(VI) and Fe(II) Interaction by a Combined Batch, Spectroscopic and DFT Calculation Investigation. *Journal of Molecular Liquids* **2021**, 337, 116365.  
<https://doi.org/10.1016/j.molliq.2021.116365>.
- (68) Joe-Wong, C.; Brown, G. E.; Maher, K. Kinetics and Products of Chromium(VI) Reduction by Iron(II/III)-Bearing Clay Minerals. *Environ. Sci. Technol.* **2017**, 51 (17), 9817–9825. <https://doi.org/10.1021/acs.est.7b02934>.
- (69) Liu, X.; Dong, H.; Zeng, Q.; Yang, X.; Zhang, D. Synergistic Effects of Reduced Nontronite and Organic Ligands on Cr(VI) Reduction. *Environ. Sci. Technol.* **2019**, 53 (23), 13732–13741. <https://doi.org/10.1021/acs.est.9b04769>.
- (70) Körner, M.; van Eldik, R. Kinetics and Mechanism of the Outer-Sphere Oxidation of Horse-Heart Cytochrome c by an Anionic Chromium(v) Complex – Kinetic Evidence for Precursor Formation and a Late Electron-Transfer Transition State. *European Journal of Inorganic Chemistry* **1999**, 1999 (10), 1805–1812. [https://doi.org/10.1002/\(SICI\)1099-0682\(199910\)1999:10<1805::AID-EJIC1805>3.0.CO;2-3](https://doi.org/10.1002/(SICI)1099-0682(199910)1999:10<1805::AID-EJIC1805>3.0.CO;2-3).
- (71) Xu, S. C.; Pan, S. S.; Xu, Y.; Luo, Y. Y.; Zhang, Y. X.; Li, G. H. Efficient Removal of Cr(VI) from Wastewater under Sunlight by Fe(II)-Doped TiO<sub>2</sub> Spherical Shell. *Journal of Hazardous Materials* **2015**, 283, 7–13. <https://doi.org/10.1016/j.jhazmat.2014.08.071>.
- (72) Dong, C.; Ji, J.; Shen, B.; Xing, M.; Zhang, J. Enhancement of H<sub>2</sub>O<sub>2</sub> Decomposition by the Co-Catalytic Effect of WS<sub>2</sub> on the Fenton Reaction for the Synchronous Reduction of

- Cr(VI) and Remediation of Phenol. *Environ. Sci. Technol.* **2018**, *52* (19), 11297–11308.  
<https://doi.org/10.1021/acs.est.8b02403>.
- (73) Xia, S.; Song, Z.; Jeyakumar, P.; Shaheen, S. M.; Rinklebe, J.; Ok, Y. S.; Bolan, N.; Wang, H. A Critical Review on Bioremediation Technologies for Cr(VI)-Contaminated Soils and Wastewater. *Critical Reviews in Environmental Science and Technology* **2019**, *49* (12), 1027–1078. <https://doi.org/10.1080/10643389.2018.1564526>.
- (74) Long, B.; Ye, J.; Ye, Z.; He, J.; Luo, Y.; Zhao, Y.; Shi, J. Cr(VI) Removal by *Penicillium Oxalicum* SL2: Reduction with Acidic Metabolites and Form Transformation in the Mycelium. *Chemosphere* **2020**, *253*, 126731.  
<https://doi.org/10.1016/j.chemosphere.2020.126731>.
- (75) Sharma, S.; Adholeya, A. Detoxification and Accumulation of Chromium from Tannery Effluent and Spent Chrome Effluent by *Paecilomyces Lilacinus* Fungi. *International Biodeterioration & Biodegradation* **2011**, *65* (2), 309–317.  
<https://doi.org/10.1016/j.ibiod.2010.12.003>.
- (76) Long, B.; Ye, B.; Liu, Q.; Zhang, S.; Ye, J.; Zou, L.; Shi, J. Characterization of *Penicillium Oxalicum* SL2 Isolated from Indoor Air and Its Application to the Removal of Hexavalent Chromium. *PLoS ONE* **2018**, *13* (1), e0191484.  
<https://doi.org/10.1371/journal.pone.0191484>.
- (77) Mu, Y.; Jiang, X.; Ai, Z.; Jia, F.; Zhang, L. Mn<sup>2+</sup> Promoted Cr(VI) Reduction with Oxalic Acid: The Indispensable Role of In-Situ Generated Mn<sup>3+</sup>. *Journal of Hazardous Materials* **2018**, *343*, 356–363. <https://doi.org/10.1016/j.jhazmat.2017.10.008>.

- (78) Pushkar, B.; Sevak, P.; Parab, S.; Nilkanth, N. Chromium Pollution and Its Bioremediation Mechanisms in Bacteria: A Review. *Journal of Environmental Management* **2021**, *287*, 112279. <https://doi.org/10.1016/j.jenvman.2021.112279>.
- (79) Mishra, S.; Bharagava, R. N. Toxic and Genotoxic Effects of Hexavalent Chromium in Environment and Its Bioremediation Strategies. *Journal of Environmental Science and Health, Part C* **2016**, *34* (1), 1–32. <https://doi.org/10.1080/10590501.2015.1096883>.
- (80) Li, H.; McKay, G. Relationships between the Physicochemical Properties of Dissolved Organic Matter and Its Reaction with Sodium Borohydride. *Environ. Sci. Technol.* **2021**, *55* (15), 10843–10851. <https://doi.org/10.1021/acs.est.1c01973>.
- (81) McAdams, B. C.; Aiken, G. R.; McKnight, D. M.; Arnold, W. A.; Chin, Y.-P. High Pressure Size Exclusion Chromatography (HPSEC) Determination of Dissolved Organic Matter Molecular Weight Revisited: Accounting for Changes in Stationary Phases, Analytical Standards, and Isolation Methods. *Environ. Sci. Technol.* **2018**, *52* (2), 722–730. <https://doi.org/10.1021/acs.est.7b04401>.
- (82) Sharma, V. K.; Filip, J.; Zboril, R.; Varma, R. S. Natural Inorganic Nanoparticles – Formation, Fate, and Toxicity in the Environment. *Chem. Soc. Rev.* **2015**, *44* (23), 8410–8423. <https://doi.org/10.1039/C5CS00236B>.
- (83) York, R.; Bell, N. G. Molecular Tagging for the Molecular Characterization of Natural Organic Matter. *Environmental science & technology* **2020**, *54* (6), 3051–3063.
- (84) Zhang, X.; Han, J.; Zhang, X.; Shen, J.; Chen, Z.; Chu, W.; Kang, J.; Zhao, S.; Zhou, Y. Application of Fourier Transform Ion Cyclotron Resonance Mass Spectrometry to Characterize Natural Organic Matter. *Chemosphere* **2020**, 127458.

- (85) Adegboyega, N. F.; Sharma, V. K.; Siskova, K. M.; Vecerova, R.; Kolar, M.; Zbořil, R.; Gardea-Torresdey, J. L. Enhanced Formation of Silver Nanoparticles in Ag<sup>+</sup>-NOM-Iron(II, III) Systems and Antibacterial Activity Studies. *Environ. Sci. Technol.* **2014**, *48* (6), 3228–3235. <https://doi.org/10.1021/es405641r>.
- (86) Guo, B.; Alivio, T. E. G.; Fleer, N. A.; Feng, M.; Li, Y.; Banerjee, S.; Sharma, V. K. Elucidating the Role of Dissolved Organic Matter and Sunlight in Mediating the Formation of Ag–Au Bimetallic Alloy Nanoparticles in the Aquatic Environment. *Environ. Sci. Technol.* **2021**, *55* (3), 1710–1720. <https://doi.org/10.1021/acs.est.0c06351>.
- (87) Lu, K.; Gardner, W. S.; Liu, Z. Molecular Structure Characterization of Riverine and Coastal Dissolved Organic Matter with Ion Mobility Quadrupole Time-of-Flight LCMS (IM Q-TOF LCMS). *Environ. Sci. Technol.* **2018**, *52* (13), 7182–7191. <https://doi.org/10.1021/acs.est.8b00999>.
- (88) Ouyang, S.; Hu, X.; Zhou, Q.; Li, X.; Miao, X.; Zhou, R. Nanocolloids in Natural Water: Isolation, Characterization, and Toxicity. *Environ. Sci. Technol.* **2018**, *52* (8), 4850–4860. <https://doi.org/10.1021/acs.est.7b05364>.
- (89) Sharma, V. K.; Ma, X.; Guo, B.; Zhang, K. Environmental Factors-Mediated Behavior of Microplastics and Nanoplastics in Water: A Review. *Chemosphere* **2021**, *271*, 129597. <https://doi.org/10.1016/j.chemosphere.2021.129597>.
- (90) Adegboyega, N. F.; Sharma, V. K.; Siskova, K.; Zbořil, R.; Sohn, M.; Schultz, B. J.; Banerjee, S. Interactions of Aqueous Ag<sup>+</sup> with Fulvic Acids: Mechanisms of Silver Nanoparticle Formation and Investigation of Stability. *Environ. Sci. Technol.* **2013**, *47* (2), 757–764. <https://doi.org/10.1021/es302305f>.

- (91) Barnie, S.; Zhang, J.; Wang, H.; Yin, H.; Chen, H. The Influence of PH, Co-Existing Ions, Ionic Strength, and Temperature on the Adsorption and Reduction of Hexavalent Chromium by Undissolved Humic Acid. *Chemosphere* **2018**, *212*, 209–218. <https://doi.org/10.1016/j.chemosphere.2018.08.067>.
- (92) Zhang, J.; Yin, H.; Chen, L.; Liu, F.; Chen, H. The Role of Different Functional Groups in a Novel Adsorption-Complexation-Reduction Multi-Step Kinetic Model for Hexavalent Chromium Retention by Undissolved Humic Acid. *Environmental Pollution* **2018**, *237*, 740–746.
- (93) Wittbrodt, P. R.; Palmer, C. D. Reduction of Cr (VI) in the Presence of Excess Soil Fulvic Acid. *Environmental Science & Technology* **1995**, *29* (1), 255–263.
- (94) Wittbrodt, P. R.; Palmer, C. D. Effect of Temperature, Ionic Strength, Background Electrolytes, and Fe(III) on the Reduction of Hexavalent Chromium by Soil Humic Substances. *Environ. Sci. Technol.* **1996**, *30* (8), 2470–2477. <https://doi.org/10.1021/es950731c>.
- (95) Chappell, J. Quantitative Analysis of Chromium(V) by EPR Spectroscopy. *Talanta* **1998**, *46* (1), 23–38. [https://doi.org/10.1016/S0039-9140\(97\)00244-0](https://doi.org/10.1016/S0039-9140(97)00244-0).
- (96) Barnie, S.; Zhang, J.; Obeng, P. A.; Duncan, A. E.; Adenutsi, C. D.; Xu, L.; Chen, H. Mechanism and Multi-Step Kinetic Modelling of Cr(VI) Adsorption, Reduction and Complexation by Humic Acid, Humic and Kerogen from Different Sources. *Environ Sci Pollut Res* **2021**, *28* (29), 38985–39000. <https://doi.org/10.1007/s11356-021-13519-z>.
- (97) Jiang, B.; Gong, Y.; Gao, J.; Sun, T.; Liu, Y.; Oturan, N.; Oturan, M. A. The Reduction of Cr(VI) to Cr(III) Mediated by Environmentally Relevant Carboxylic Acids: State-of-the-

Art and Perspectives. *Journal of Hazardous Materials* **2019**, 365, 205–226.

<https://doi.org/10.1016/j.jhazmat.2018.10.070>.

## CHAPTER 2

### Interaction of peroxyacetic acid with chromium(III):

#### Understanding degradation of coexisting organic pollutants in water

##### 2.1. Introduction

Studies on peroxyacetic acid ( $\text{CH}_3\text{C}(\text{O})\text{OOH}$ , PAA) are continued to increase due to its potential as disinfectant and oxidant in treating water. PAA is an alternative to chlorination disinfection because of its promising sterilization ability, feasible implementation, and decrease formation of toxic chlorinated disinfection by-products (DBPs).<sup>1</sup> PAA has demonstrated inactivation of virus, bacteria, and spores and has been applied as disinfectant in health care facilities and pulp and paper and food industries.<sup>2-4</sup> PAA has also emerged an effective oxidant ( $E_h^0 = 1.0-1.96$  V versus SHE) in advanced oxidation processes (AOPs).<sup>1</sup> PAA has potential to oxidize a wide range of organics in water, however, it is not able to degrade recalcitrant pollutants due to high selectivity.<sup>1</sup> Research is forthcoming on the application of the combination of PAA with low-valent and high-valent transition metal ions to enhance the degradation of pollutants in water. Examples of added metal ion include Fe(II), Co(III), Ru(III), and Fe(VI).<sup>5-8</sup> The results of these studies made us to think how the effectiveness of PAA as an oxidant would be in degrading organic pollutants in presence of already existed metal ions in water. The present study thus examines if the interaction of PAA with chromium(III) (Cr(III)) in water has any role in oxidizing coexisting organic pollutants in water.

Sources of Cr are primarily from waste of industrial activities such as coal-fired power production, chrome pigment production, wood preservation, stainless steel and cement



production, galvanization, electroplating, and leather tanning.<sup>9,10</sup> Additional input of Cr in wastewater might also be from dietary supplements of Cr(III).<sup>11,12</sup> The concentration of Cr in industrial wastewater can be up to 3.86 mM.<sup>13</sup> The toxicity of Cr is highly dependent on its oxidation state; Cr(VI) is a known carcinogen and Cr(III) is significantly less toxic.<sup>14</sup> Reduction of Cr(VI) to the Cr(III) has been well-studied for remediating Cr-contaminated systems.<sup>15-17</sup> Despite this, trace levels of Cr(III) in wastewater must still be carefully dealt with, as oxidation to Cr(VI) has been shown by chlorine, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and ozone which may produce reactive, intermediate complexes of Cr(IV) and/or Cr(V).<sup>18-21</sup> Significantly, the intermediate Cr species are reactive with organic compounds and may mitigate the remediation of coexisting organic pollutants present in water.<sup>19,22,23</sup> This promoted us to explore if PAA could result in such intermediate Cr species and subsequently degrade pharmaceuticals in water.

A major fraction of pharmaceuticals in conventional wastewater treatment have incomplete removals and enter water resources, leading to environmental and human health concern.<sup>24,25</sup> Antibiotics are among the most prevalent pharmaceuticals found in the environment because of their wide application in human and veterinary medicine along with agriculture purposes.<sup>26,27</sup> Detection of antibiotics in wastewater effluent has ranged from trace levels up to µg/L.<sup>25,28</sup> The primary threats of antibiotics in the environment stems from the potential of altered ecosystems and antibiotic-resistant genes (ARGs) and bacteria (ARB).<sup>25,27,29</sup> Health concern surrounding ARGs and ARB arises from a decrease of therapeutic potential against human and animal pathogens.<sup>27</sup> Out of many antibiotics, trimethoprim (5-(3, 4, 5-trimethoxybenzyl)pyrimidine-2,4-diamine, TMP), is frequently detected in wastewater effluent.<sup>25,28,30</sup> TMP is often given in pair with sulfonamides to treat various infections.<sup>31,32</sup> A substantial portion of TMP that is excreted in urine keeps its antibiotic properties; about 10% -

30% of TMP is metabolized to an inactive form.<sup>32</sup> Its antibiotic properties are attributed to the 2,4-diaminopyrimidine (DAP) moiety.<sup>26</sup> The focus of this study is therefore, mainly on investigating the degradation of TMP during the interaction of PAA with Cr(III).

The objectives of the paper are: (i) study the degradation of TMP under different experimental conditions (concentrations of PAA and Cr(III) and pH), (ii) learn degradation of other pharmaceuticals (enrofloxacin (ENR), sulfamethoxazole (SMX), carbamazepine (CBZ), and ibuprofen (IBU)), (iii) explore reactive species causing the degradation of TMP in the PAA-Cr(III) system, and (iv) identify the oxidized products (OPs) of TMP.

## **2.2. Experimental Methods**

### *2.2.1. Chemicals and reagents*

Trimethoprim (TMP, > 98.0%), sulfamethoxazole (SMX, > 98.0%), and enrofloxacin (ENR, > 98.0%) were purchased from Tokyo Chemical Industry (Portland, USA). Sodium chromate tetrahydrate (Cr(VI), 99%), peracetic acid solution (PAA, 32 wt. % in dilute acetic acid), methanol (HPLC grade,  $\geq$  99.9%), carbamazepine (CBZ) was purchased from Sigma-Aldrich (St. Louis, USA). Sodium phosphate dibasic anhydrous, sodium thiosulfate, acetic acid (glacial), o-phosphoric acid (85%) and L-ascorbic acid (Asc, assay 99.8%) were purchased from Fisher-Scientific (Fair Lawn, USA). Hydrogen peroxide solution 50% was purchased from HACH Company World Headquarters (Loveland, USA). Methyl phenyl sulfoxide (PMSO, 98+%) was purchased from Acros Organics (New Jersey, USA) and methyl phenyl sulfone (PMSO<sub>2</sub>, 98+%) was purchased from Alfa Aesar (Ward Hill, USA). Distilled water used in solutions were obtained from > 18.2 M $\Omega$ -cm Milli-Q Millipore Direct 8 water purification system (Millipore Sigma, Burlington, USA).

### 2.2.2. Removal experiments

Initial experiment concentrations of PAA, H<sub>2</sub>O<sub>2</sub>, acetic acid (AcA), Cr(III), and pollutants were 1.315 mM, 520.5 μM, 2.055 mM, 13.15 – 1315 μM, and 5.0 μM, respectively. The experimental ratios for [PAA]/[Cr(III)] ranged from 100 to 1 for pollutant degradation experiments at 1.0 and 2.0 hours. Initial concentrations for analyzing TMP degradation in the PAA/Cr(VI) system were [PAA] = 100.0 μM, [Cr(VI)] = 5.0 – 1000.0 μM, and 5.0 μM TMP. 10.0 mM Na<sub>2</sub>HPO<sub>4</sub> was used as the buffer for all solutions and adjusted to desired pH. The pH was measured by an Accumet AE150 pH meter (Westford, USA). Additionally, a 13 mm syringe filter (with 0.2 μm PTFE membrane) was used for filtering solutions with noticeable insoluble Cr into HPLC vials. 10.0 μL of 13.0 mM Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added to all HPLC vials to quench the reaction at desired times. The pollutant concentration was then analyzed by HPLC.

The reduction of Cr(VI) by ascorbic acid (Asc) was designed to identify if Cr-intermediate species may be responsible for TMP degradation. Initial experiment concentrations of Cr(VI), Asc, and TMP were 25.0 – 500.0 μM, 500.0 μM, and 5.0 μM respectively. 10.0 mM Na<sub>2</sub>HPO<sub>4</sub> was adjusted to pH 7.0 and used for buffering all solutions. When Asc was used in place of PAA, the Na<sub>2</sub>HPO<sub>4</sub> buffer was purged with N<sub>2</sub> for up to 15 minutes to analyze potential interference of Asc autoxidation with the reduction of Cr(VI); this was analyzed by UV-visible absorbance. Before sample collection for TMP degradation, 10.0 μL of 13.0 mM Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added to all HPLC vials to quench the reaction at desired time. Samples were taken at 1.0 hour and TMP concentration was analyzed by HPLC.

### 2.2.3. Quenching experiments

Radical quenchers were used to probe for reactive species present in experiments mentioned. Benzoic acid (BA) was used to quench  $\bullet\text{OH}$  and was prepared at an initial concentration of 13.15 mM which was 2,360 times higher than pollutant concentration. 2,4-hexadiene was used to quench  $\bullet\text{OH}$  and PAA radicals and was an initial concentration of 5.0 mM which is 1000 times the concentration of TMP. Fresh preparation of BA and 2,4-HD were made separately in 10.0 mM  $\text{Na}_2\text{HPO}_4$  buffered at pH 8.0. Conditions for both BA or 2,4-HD quenching experiments included 1.315 mM PAA, 13.15 – 1315  $\mu\text{M}$  Cr(III), and 5.0  $\mu\text{M}$  TMP. Additionally, methyl phenyl sulfoxide (PMSO) can be oxidized to methyl phenyl sulfone (PMSO<sub>2</sub>) selectively by high-valent metal intermediate species like Cr(V).<sup>22</sup> PMSO initial concentration was 200.0  $\mu\text{M}$ , with 263.0  $\mu\text{M}$  Cr(III), and 1.315 mM PAA, and samples were collected every 30 minutes for 2.0 hours.

### 2.2.4 Analytical methods

#### 2.2.4.1 High Performance Liquid Chromatography

The concentrations of pollutants in samples from the experiments mentioned were measured with a Thermo Scientific UltiMate 3000 UHPLC+ with a Restek Ultra C18 5 $\mu\text{m}$  (250 x 4.5 mm) column. Column temperature was maintained at 30°C for all experiments. Instrument methods for pollutants were as follows in binary mobile phase of Solvent A (water with 5%  $\text{H}_3\text{PO}_4$ ) and Solvent B (methanol): TMP – 75% A and 25% B at flow rate of 1 mL min<sup>-1</sup> and 271 nm; IBP – 21% A and 79% B at flow rate of 0.8 mL min<sup>-1</sup> and 223 nm; ENR – 68% A and 32% B at flow rate of 0.8 mL min<sup>-1</sup> and 271 nm; SMX – 60% A and 40% B at flow rate of 0.8 mL min<sup>-1</sup> and 290 nm; CBZ – 40% A and 60% B at a flow rate of 0.8 mL min<sup>-1</sup> and 284 nm; PMSO

and PMSO<sub>2</sub> – 81% A and 19% B at flow rate of 1.0 mL min<sup>-1</sup> and 230 nm (PMSO) and 215 nm (PMSO<sub>2</sub>).

#### *2.2.4.2 UV-Visible Absorbance*

Absorbance analysis using a Thermo Scientific BioMater 3S UV-Visible Spectrophotometer was used to monitor the change in absorbance of Cr(III) and Cr(VI) and Asc. Measurements were taken for Cr(III) and Cr(VI) at desired times from 0.0 to 2.0 hours at different conditions; these conditions depended on concentration of Cr and PAA as well as pH. In the UV-Visible experiment of Cr(VI) and Asc, measurements were taken within 1.0 h for 500.0 μM of both Cr(VI) and Asc at pH 7.0 to compare the effect of purging N<sub>2(g)</sub> into the 10.0 mM phosphate buffer.

#### *2.2.4.3 Electron paramagnetic resonance (EPR) spectroscopy*

A Bruker Elexsys-II E500 spectrometer equipped with a standard resonator and a CoolEdge cryo system (Billerica, USA) was used to probe the signal of •OH. The operating parameters of EPR were: 9.4 GHz frequency (X-band), 20.0 mW microwave power, 9.8 GHz microwave frequency, 1.00 G modulation amplitude, 100 kHz modulation frequency, 120.0 G sweep width, 3340.0 G center field, 30.0 s sweep time, 20 scan times, and 25.0 dB attenuation. The concentration of 5,5-dimethyl-1-pyrroline N-oxide (DMPO, purchased from Sigma-Aldrich (St. Louis, USA)) as the spin trapper for •OH was 50.0 mM. The reaction solutions were injected into a 2 mm quartz EPR tube using a syringe needle, placed into a 4 mm quartz EPR tube, and then measured by EPR immediately.

## 2.3. Results and Discussion

### 2.3.1. Degradation of pollutants by PAA-Cr(III) system

Initially, experiments were conducted on the degradation of TMP by PAA-Cr(III) at pH 6.0 by varying the concentrations of Cr(III) (13.15 – 1315  $\mu\text{M}$ ) while keeping PAA concentration constant at 1315  $\mu\text{M}$ . Similar experiments were also performed using only  $\text{H}_2\text{O}_2$  and acetate because these are inherently present in the solution of PAA (i.e.,  $\text{CH}_3\text{C}(\text{O})\text{OH} + \text{H}_2\text{O}_2 \rightleftharpoons \text{CH}_3\text{C}(\text{O})\text{OOH} + \text{H}_2\text{O}$ ). As shown in Fig. 2.1 and Fig. 2.2, no significant degradation was noticeable under different conditions. This suggests that no reactive species in PAA-Cr(III) solution existed at pH 6.0 to result in oxidation of TMP.

Next, the pH of the mixed solution of TMP-Cr(III)-PAA was raised to pH 8.0 at a molar ratio of 5:1 ([PAA]:[Cr(III)]) and the degradation of TMP was followed as a function of time (Fig. 2.3). PAA alone was able to react slowly and up to 20% degradation was seen in 5.0 h (Fig. 2.3a). Significantly, Cr(III)-PAA could degrade TMP to almost 90% in 5.0 h (Fig. 2.3b). This indicates that the increase in pH to alkaline medium had sufficient reactive species to oxidize TMP. When pH of the reactant solution was increased to pH 9.0 and 10.0, slight increase (i.e., up ~5%) in the oxidation of TMP by PAA and Cr(III)-PAA was observed (Fig. 2.3). TMP has an equilibrium with two acid dissociation constants ( $\text{H}_2\text{TMP}^{2+} \rightleftharpoons \text{H}^+ + \text{HTMP}^+$ ,  $\text{p}K_{\text{a}1} = 3.2$ ;<sup>33</sup> and  $\text{HTMP}^+ \rightleftharpoons \text{H}^+ + \text{TMP}$ ,  $\text{p}K_{\text{a}2} = 7.2$ <sup>34</sup>). In the pH range of 8.0 – 10.0, TMP was mostly in the neutrally charged species (i.e., 84.2 – 99.9%). PAA has acid-base equilibrium ( $\text{CH}_3\text{C}(\text{O})\text{OOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{C}(\text{O})\text{OO}^-$ ;  $\text{p}K_{\text{a}} = 8.2$ ) and fractions of the possible oxidant species of PAA (i.e.,  $\alpha(\text{CH}_3\text{C}(\text{O})\text{OOH})$  and  $\alpha(\text{CH}_3\text{C}(\text{O})\text{OO}^-)$ ), vary with pH.<sup>1</sup> For example,  $\alpha(\text{CH}_3\text{C}(\text{O})\text{OOH})$  and  $\alpha(\text{CH}_3\text{C}(\text{O})\text{OO}^-)$  at pH 8.0 are 63.1% and 36.9%, respectively, which changed to 1.6% and 98.4%, respectively, at pH 10.0. It appears that a little decrease in levels of TMP by PAA with

almost no pH dependence may be carried out by the reactions of TMP with both oxidant species of PAA (Fig. 2.3a).

The results of the increase in oxidation of TMP for PAA-Cr(III) with an increase in pH from 6.0 to 8.0 may be described by considering increasing reactivity of Cr(III) with PAA to yield oxidative species that reacted with TMP. Chromium(III) exists in different hydroxo species in the acidic to basic pH range. Generally, four hydroxo species,  $\text{CrOH}^{2+}$ ,  $\text{Cr(OH)}_2^+$ ,  $\text{Cr(OH)}_3^0$ , and  $\text{Cr(OH)}_4^-$  are present, based on the equilibrium constants (reactions 1-5).<sup>35</sup>



A plot of fraction of Cr(III) species with pH (Fig. 2.4) suggests that the fractions of  $\text{CrOH}^{2+}$ ,  $\text{Cr(OH)}_2^+$ , and  $\text{Cr(OH)}_3^0$  are 60%, 30% and 10% at pH 6.0. However, at pH 8.0,  $\text{Cr(OH)}_3^0$  is the dominating species ( i.e., > 90%) and not much change in this fraction happens when the pH was changed from 8.0 to 9.0 and 10.0 (see Fig. 2.4). It seems that of the several Cr(III) species,  $\text{Cr(OH)}_3^0$  could react with PAA to produce oxidative species that reacted with TMP. The rates of this reaction would not change with pH because concentration of  $\text{Cr(OH)}_3^0$  is not varied in the pH range of 8.0 – 10.0. Therefore, degradation of TMP by PAA-Cr(III) in the pH range of 8.0 – 10.0 did not influence much by the pH (see Fig. 2.3b).

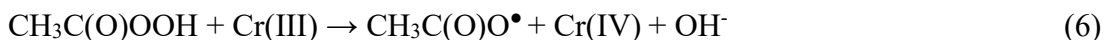
In next set of experiments, a role of  $\text{H}_2\text{O}_2$  present in PAA was investigated. In this study, the concentration of Cr(III) was varied at pH 8.0 and degradation of TMP was monitored at 2.0

h; the results are shown in Fig. 2.5. The H<sub>2</sub>O<sub>2</sub>-Cr(III) system could also degrade TMP, and the maximum degradation was ~40% at a molar ratio of 2:1 ([H<sub>2</sub>O<sub>2</sub>]:[Cr(III)]). Comparatively, PAA-Cr(III) had the maximum degradation was ~60% at a molar ratio of 5:1 ([PAA]:Cr(III)). It should be pointed out that in the mixed solution of PAA and Cr(III) at a molar ratio of 5:1, the molar ratio of H<sub>2</sub>O<sub>2</sub> to Cr(III) was 2:1. The results suggest that the PAA-Cr(III) had additional oxidant species compared to oxidant(s) in H<sub>2</sub>O<sub>2</sub>-Cr(III) to have higher degradation of TMP (Fig. 2.5). The results further showed that the optimum degradation of TMP at pH 8.0 was at a molar ratio of 5:1 ([PAA]:[Cr(III)]). Interestingly, this was the condition applied in our earlier experiments (see Fig. 2.3).

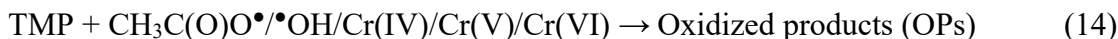
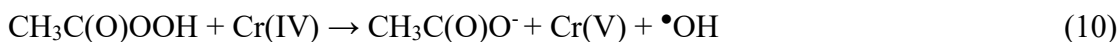
The Cr(III)-PAA system at pH 8.0 was further explored to determine if other co-pollutants could be degraded having different molecular structures (Table 2.1). Removal of other contaminants under the same conditions as Fig. 2.3 revealed an enhanced degradation compared to PAA alone (Fig. 2.6). However, the magnitude of increased oxidation depended on the moieties present in each of the pollutants. Sulfonamide containing pollutants, SMX and TMP, had the highest increase in degradation. ENR reacted with both PAA and PAA-Cr(III). Significantly, CBZ and IBU had no reactivity with PAA; however, a slight increase in degradation was observed (Fig. 2.6) by adding Cr(III) (i.e., PAA-Cr(III)).

### 2.3.2. Reactive species study

When PAA interacts with Cr(III), a series of reactions may take place that generate different oxidative species, Cr(IV), Cr(V), Cr(VI), CH<sub>3</sub>C(O)O•, and •OH, (reactions 6-10). The produced species then possibly react with pollutants like TMP to degrade it.







Studies were performed to determine which of the oxidative species involved caused the degradation of TMP at pH 8.0. Initially, the formation of Cr(VI) in the mixed PAA and Cr(III) was investigated. The mixed solution had a representative spectra of Cr(VI) (Fig. 2.7), suggesting the formation of Cr(VI) in the reaction of Cr(III) with PAA through the sequence of reactions (reactions 6-14). The reaction of PAA with Cr(III) must be going through the formation of Cr(IV)/Cr(V) prior to the generation of Cr(VI). The formed Cr(VI) may react with TMP to oxidize it. Experiments were then conducted independently by mixing the solutions of Cr(VI) and TMP at pH 8.0. No apparent decrease in absorbance of Cr(VI) was observed (Fig. 2.8). Furthermore, no significant decrease in the TMP by Cr(VI) mixed solution was observed (Fig. 2.9). Results suggest that Cr(VI) did not oxidize TMP at pH 8.0. Overall, Cr(VI) that was formed in the reaction of Cr(III) with PAA had no role in degrading TMP by PAA-Cr(III) at pH 8.0 (see Fig. 2.3).

Next, we investigated the possibility of Cr(V)/Cr(IV) to oxidize TMP. In this set of experiments, we used the known chemistry of Cr(VI) with ascorbic acid (Asc) that generates Cr(V) from the reaction of  $\text{Cr(VI)} + \text{Asc} \rightarrow \text{Cr(V)} + \text{Asc}\bullet$ .<sup>34</sup> Initially, measurements were made to learn if dissolved oxygen in the Cr(VI)-Asc system had a significant impact on the autoxidation of Asc and subsequently the reduction of Cr(VI); this was done by purging  $\text{N}_2(\text{g})$

into the system for up to 15 minutes. The results (Fig. 2.10) indicated almost no change in absorbance at 265 nm (i.e., Asc) and 372 nm (i.e., Cr(VI)) from N<sub>2(g)</sub> purge (noted as “No O<sub>2</sub>”) over 1.0 hour. This suggests that Cr acts as a catalyst, outcompeting the autoxidation of Asc by dissolved oxygen; thus, dissolved oxygen does not interfere with our reaction of Cr(VI) with ascorbic acid.<sup>38</sup> Next, TMP was mixed with a solution of Cr(VI) and ascorbic acid and the concentration of TMP was monitored with time (Fig. 2.11). The decrease in TMP concentration was observed; suggesting that formed Cr(V) could react with TMP. It is possible that Cr(V) could also react with ascorbic acid to yield Cr(IV), which may also be reacting with TMP. The generated Asc• has usually no reactivity with organic compounds, therefore, both Cr(V)/Cr(IV) may be oxidizing TMP.<sup>39</sup> Results of this study indicate that Cr(V)/Cr(IV) species have a role in oxidizing TMP by PAA-Cr(III).

The involved CH<sub>3</sub>C(O)O•/CH<sub>3</sub>C(O)OO• and •OH species in PAA-Cr(III) were investigated at pH 8.0. The 2,4-HD as a probe molecule of these species was utilized in a concentration of 5.0 mM which was 1000 times the concentration of TMP. The C=C double bond in 2,4-HD allows for quenching of acetyl(per)oxyl radicals (i.e., CH<sub>3</sub>C(O)O• and CH<sub>3</sub>C(O)OO•).<sup>8</sup> Notably, a rate constant of  $9.2 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$  was observed between CH<sub>3</sub>C(O)OO• and a C=C containing compound (β-carotene) in benzene.<sup>40</sup> Additionally, the rate constant observed for 2,4-HD and •OH has been reported to be  $k = 9.16 \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$ .<sup>41</sup> The use of 2,4,-HD in the mixed solution of TMP-PAA-Cr(III) decreased the degradation of TMP compared to no 2,4-HD (Fig. 2.12); indicating that both CH<sub>3</sub>C(O)O•/CH<sub>3</sub>C(O)OO• and •OH species may be causing the degradation of TMP. To distinguish between PAA radicals and •OH, benzoic acid (BA) was applied to the solution of TMP-PAA-Cr(III). BA has much higher reactivity with •OH ( $k \approx 4.66 \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$ ) than that with CH<sub>3</sub>C(O)OO• ( $k'_{\text{PAA}} \approx 4.18 \times 10^4 \text{ s}^{-1}$ ).

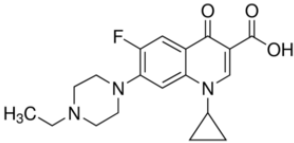
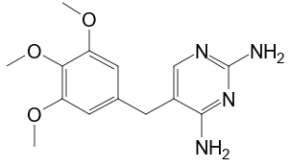
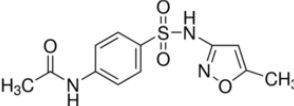
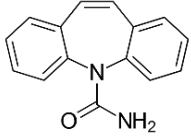
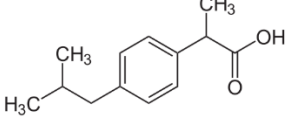
<sup>1</sup>).<sup>6,42</sup> As shown in Fig. 2.12, miniscule difference in the degradation of TMP by the two systems falls within experimental error (i.e., either the addition of 2,4-HD or BA). Results of Fig. 2.12 suggest that between the two species,  $\bullet\text{OH}$  was the degrading the responsible oxidant to degrade TMP.

Additionally, the formation of  $\bullet\text{OH}$  was further confirmed by EPR in conditions coinciding with our observation of highest TMP degradation. Noted in Fig. 2.13, no signal was observed for Cr(III),  $\text{H}_2\text{O}_2$ , and PAA solutions alone. In contrast, clear signal of the 1:2:2:1 peaks was observed for in both the  $\text{H}_2\text{O}_2$ -Cr(III) and PAA-Cr(III) systems, which indicated the formation of DMPO- $\bullet\text{OH}$  adduct. Significantly, the signal intensity of DMPO- $\bullet\text{OH}$  was markedly stronger in PAA-Cr(III) than in  $\text{H}_2\text{O}_2$ -Cr(III). This directly relates to Fig. 2.5, indicating that an increase in TMP degradation by PAA-Cr(III) compared to that of  $\text{H}_2\text{O}_2$ -Cr(III) is significantly due to the presence of  $\bullet\text{OH}$ .

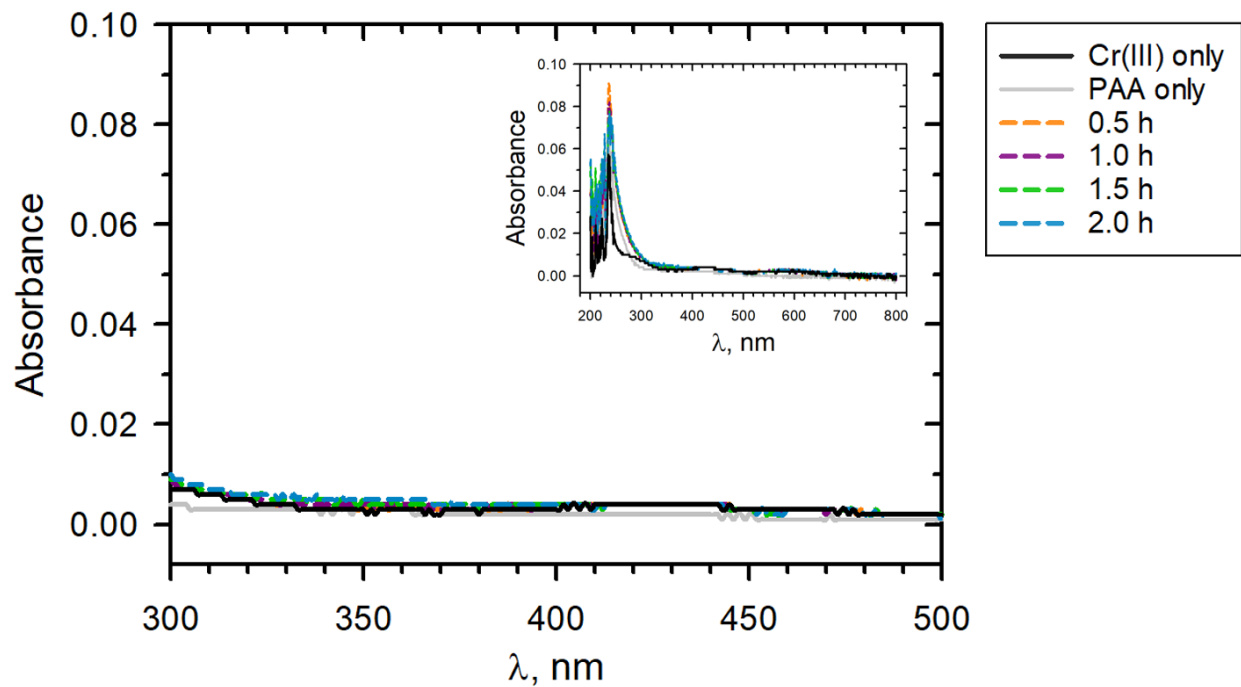
Lastly, an effort to directly detect Cr-intermediates for the remaining degradation of TMP not attributed to  $\bullet\text{OH}$  was carried out. Oxidation of methyl phenyl sulfoxide (PMSO) to methyl phenyl sulfone ( $\text{PMSO}_2$ ) has been used previously to selectively determine the presence of high-valent metal ion intermediate species such as Fe(V), Ru(V), Co(IV), and Cr(V).<sup>8,22,43,44</sup> The results in Fig. 2.14 indicate that PAA can oxidize PMSO over 2.0 hours and appear to have no difference in PMSO oxidation compared to that by PAA-Cr(III). However, from previous experiments, PAA is being consumed in electron transfer steps as Cr(III) becomes oxidized to Cr(VI). Therefore, we would expect that oxidation of PMSO by PAA-Cr(III) to be less than that of PAA alone since PAA would be consumed by Cr(III). We postulate that the role of Cr(V) in the PAA-Cr(III) system likely aids in oxidation of PMSO, making it comparable to PAA alone.

## 2.4. List of Table

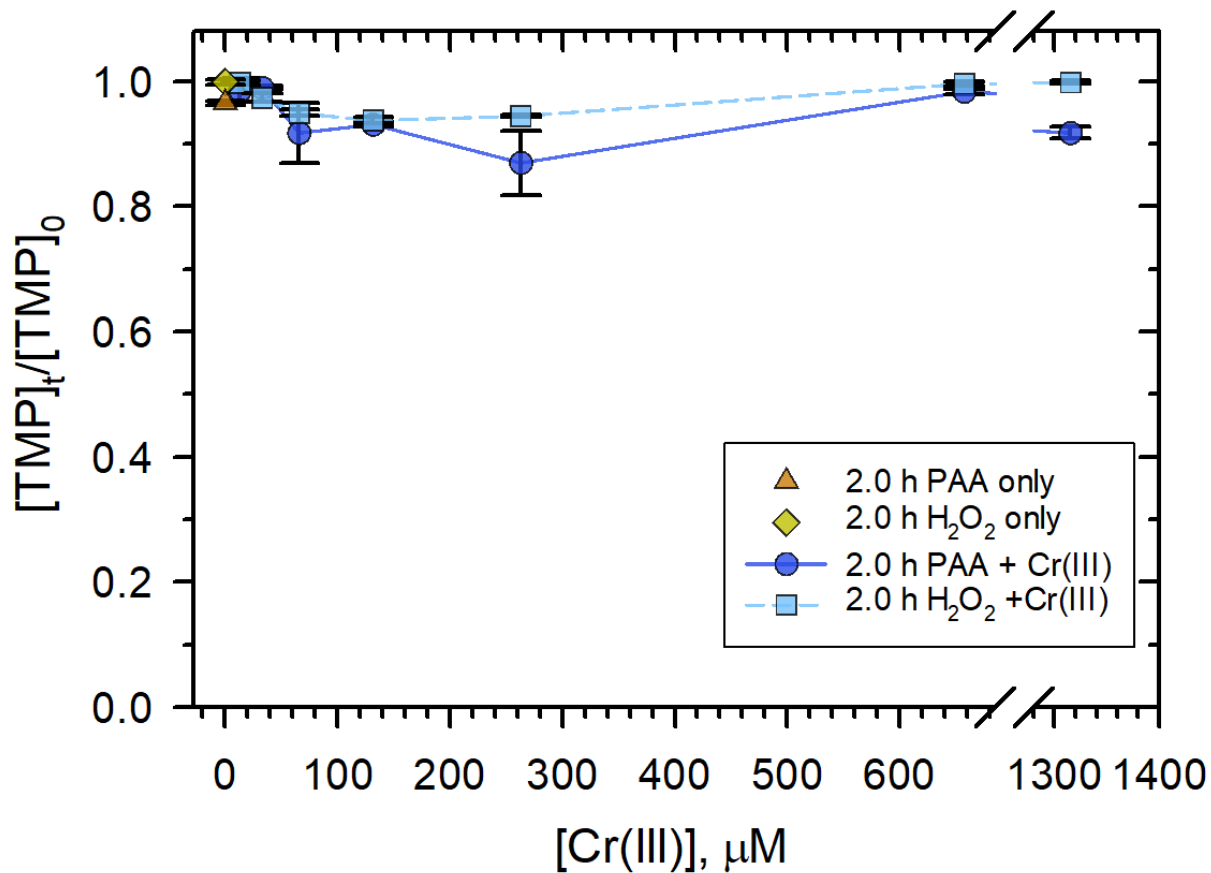
**Table 2.1.** Chemical properties of pharmaceuticals used in degradation experiments.

Compound	Function	$pK_a$ (25°C)	$\log K_{ow}$	Water	Molecular	Molecular structure
				solubility (mg L <sup>-1</sup> at 25 °C)	weight (g mol <sup>-1</sup> )	
Enrofloxacin (ENR)	Antibiotic	6.19, 7.75	0.39	146.0	359.39	
Trimethoprim (TMP)	Antibiotic	3.2, 7.2	0.91	400.0	290.32	
Sulfamethoxazole (SMX)	Antibiotic	1.6, 5.7	0.89	610.0 (at 37°C)	253.28	
Carbamazepine (CBZ)	Anticonvulsant	13.9	2.45	18.0	236.27	
Ibuprofen (IBU)	Anti-inflammatory	4.91	3.97	21.0	206.28	

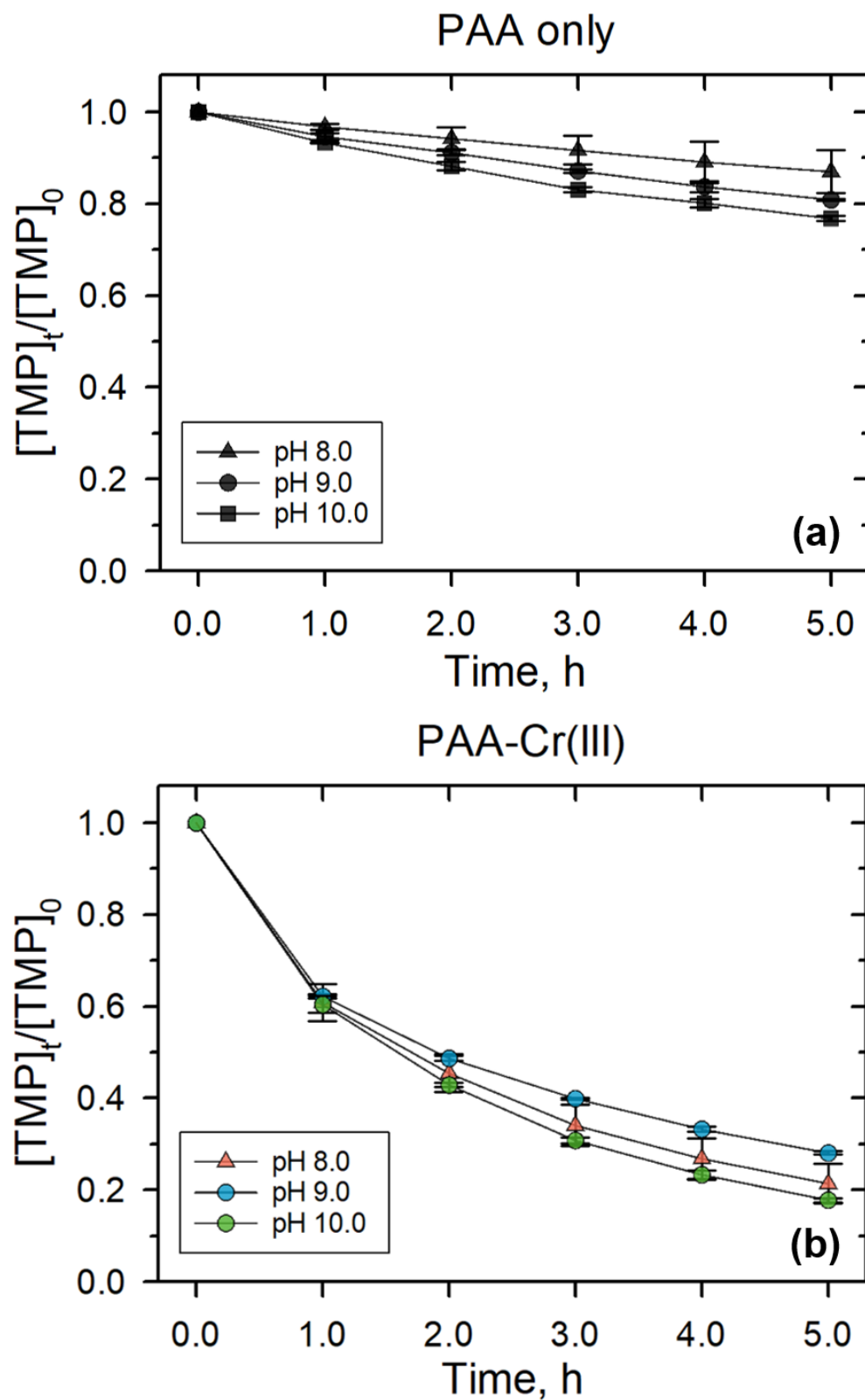
## 2.5. List of Figures



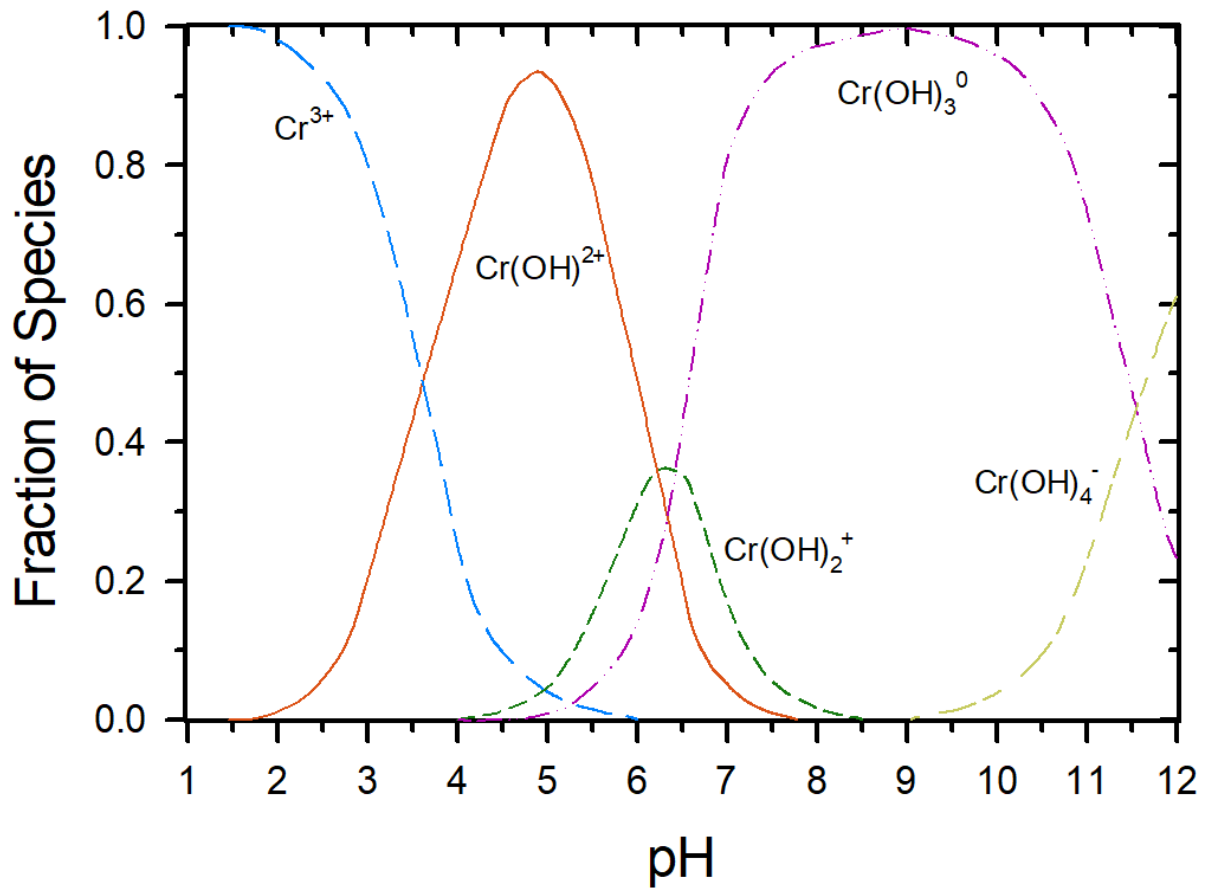
**Fig. 2.1.** UV-Visible spectra of the mixture of PAA and Cr(III) collected at different time at pH 6.0. (Experimental conditions: [PAA] = 1315.0  $\mu\text{M}$ ; [Cr(III)] = 100.0  $\mu\text{M}$ ; [Na<sub>2</sub>HPO<sub>4</sub>] = 10.0 mM)



**Fig. 2.2.** Degradation of TMP at different concentrations Cr(III) at pH 6.0 with oxidants H<sub>2</sub>O<sub>2</sub> or PAA. (Experimental condition: [TMP] = 5.0 μM, [Cr(III)] = 13.15 – 1315 μM, [PAA] = 1315.0 μM, [H<sub>2</sub>O<sub>2</sub>] = 520.5 μM; [Na<sub>2</sub>HPO<sub>4</sub>] = 10.0 mM)

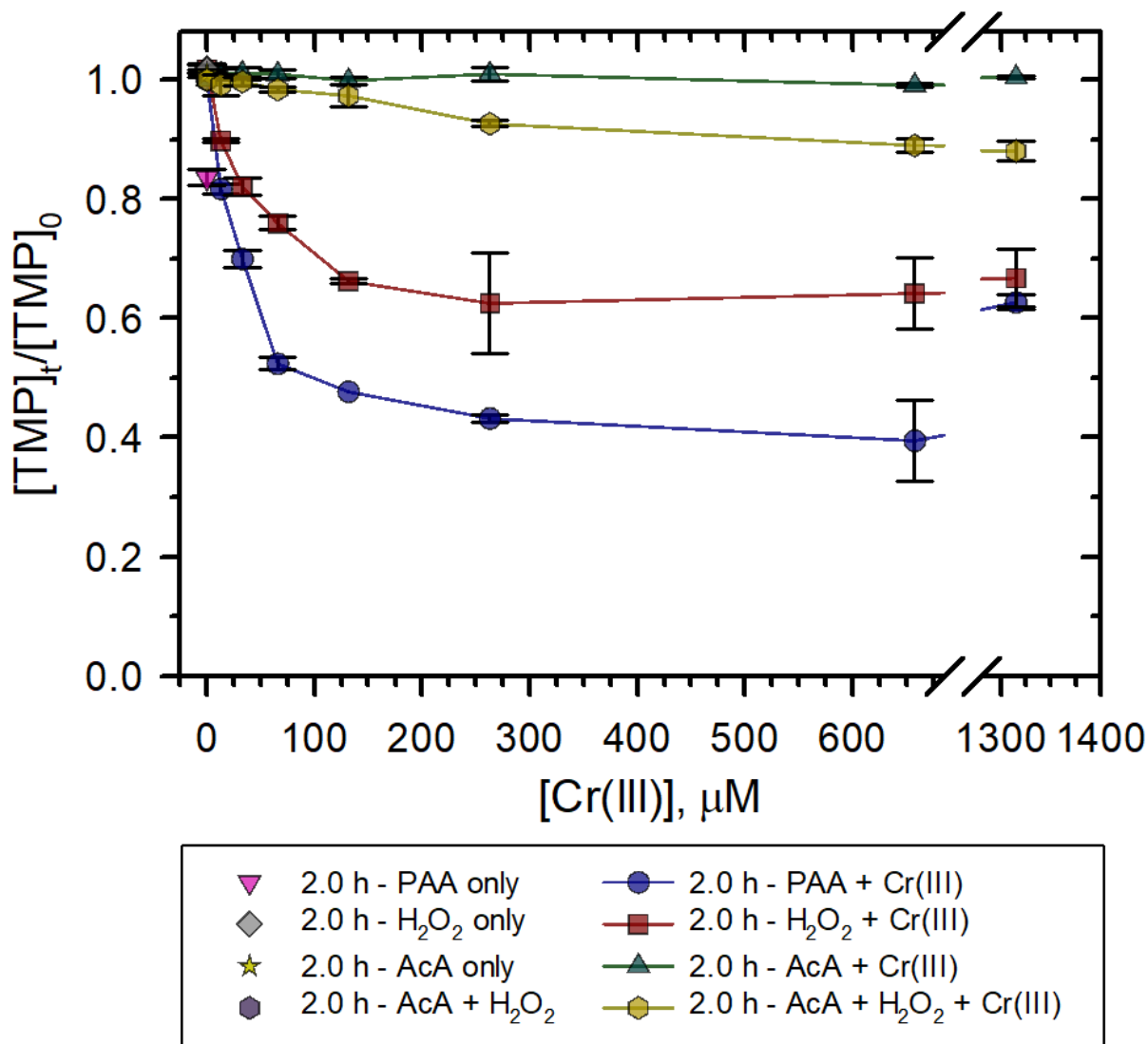


**Fig. 2.3.** Degradation of 5.0  $\mu\text{M}$  TMP over 5.0 hours at pH 8.0, 9.0, and 10.0 with  $[\text{Cr(III)}] = 263.0 \mu\text{M}$  and  $[\text{PAA}] = 1315.0 \mu\text{M}$  and  $[\text{Na}_2\text{HPO}_4] = 10.0 \text{ mM}$ .

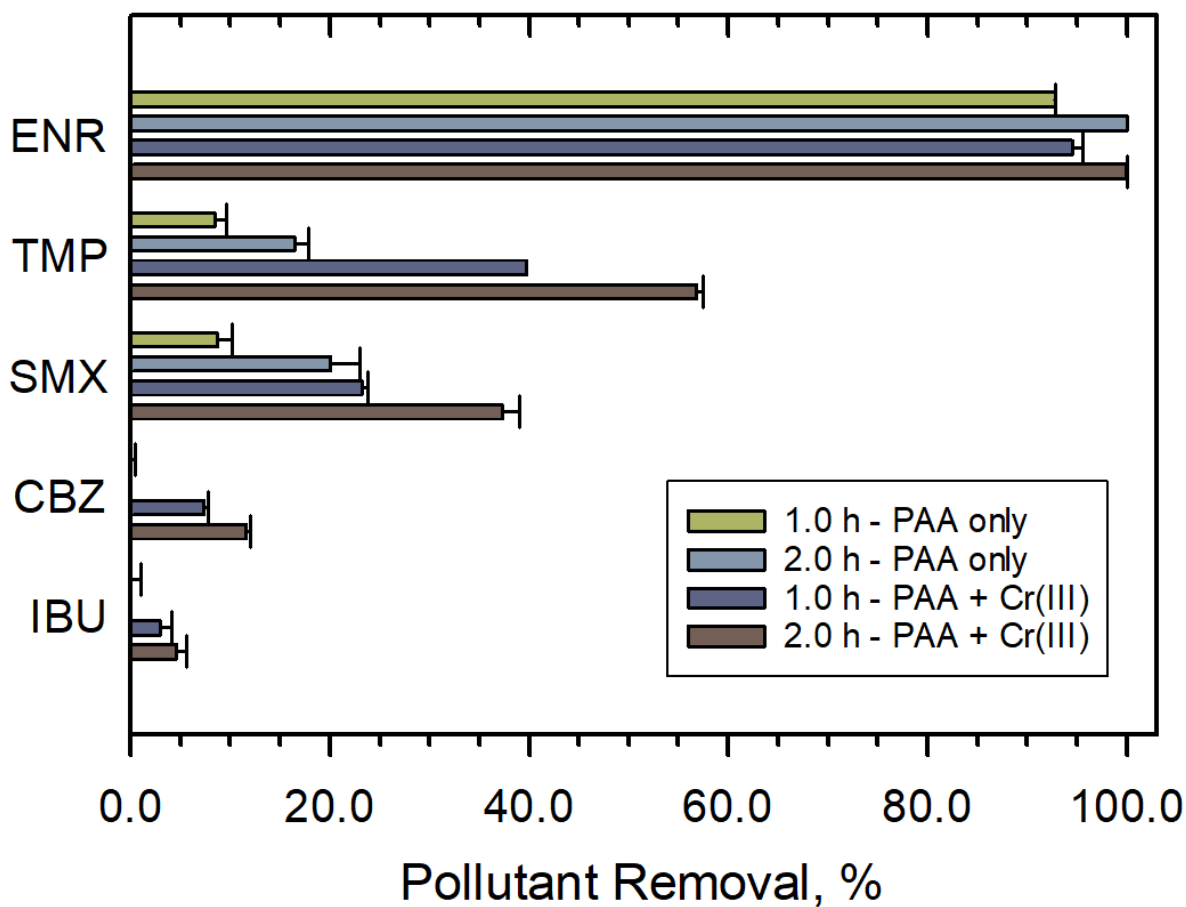


**Fig. 2.4.** Fraction of Cr(III) species as a function of pH with solution in equilibrium with Cr(OH)<sub>3</sub> (s). Redrawn from <sup>45</sup>.

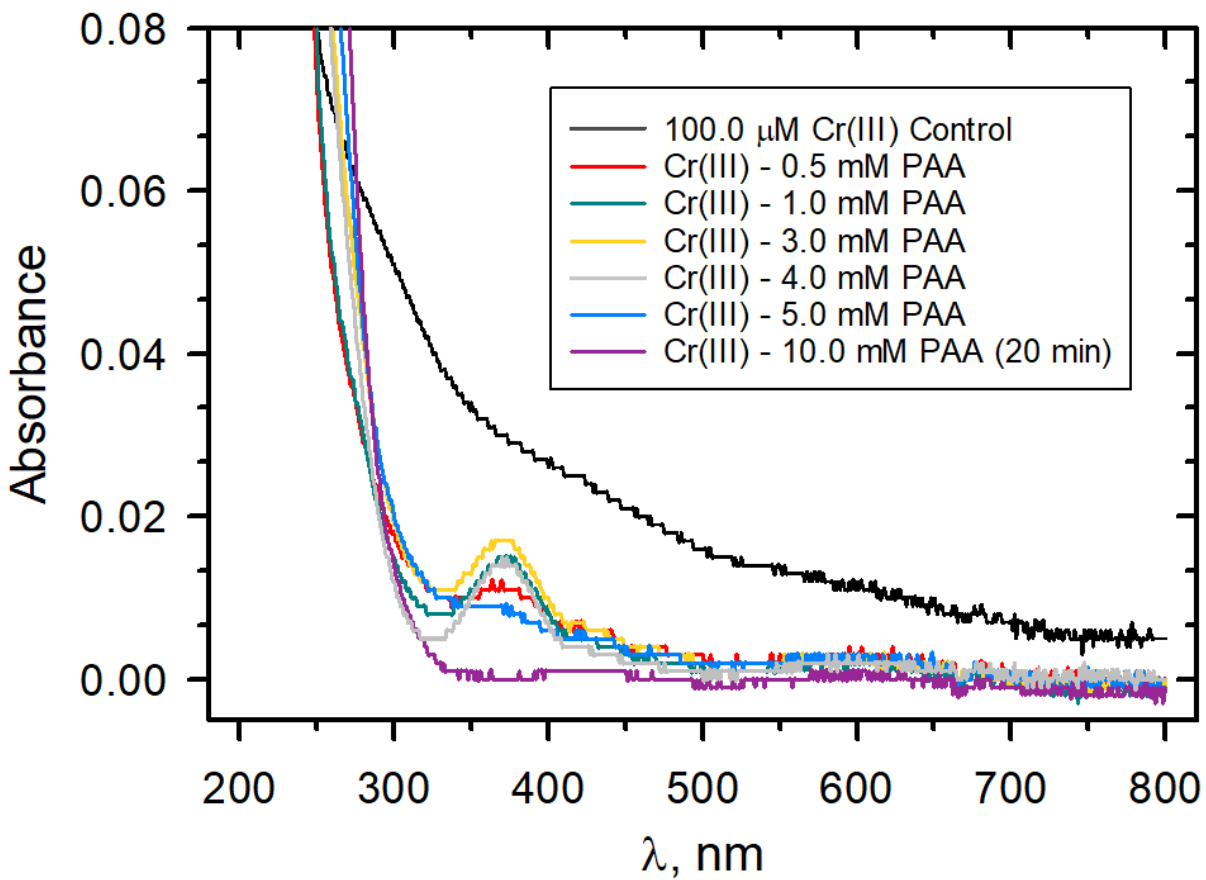




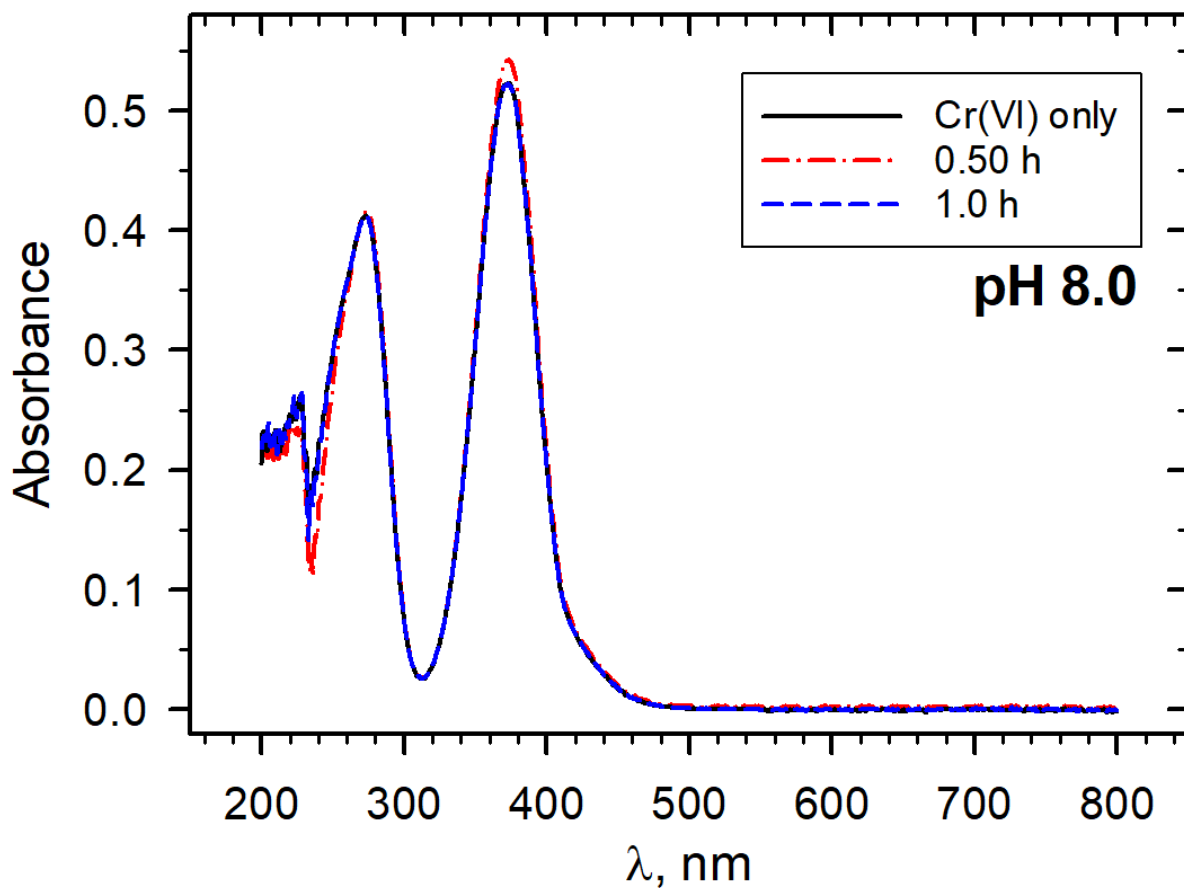
**Fig. 2.5.** Degradation of TMP in 2.0 hours at pH 8.0 indicating that PAA-Cr(III) yields the highest degradation compared to all other systems. (Experimental condition: [TMP] = 5.0 μM, [Cr(III)] = 13.15 – 1315 μM, [PAA] = 1315.0 μM, [H<sub>2</sub>O<sub>2</sub>] = 520.5 μM; [AcA] = 2.055 mM; [Na<sub>2</sub>HPO<sub>4</sub>] = 10.0 mM)



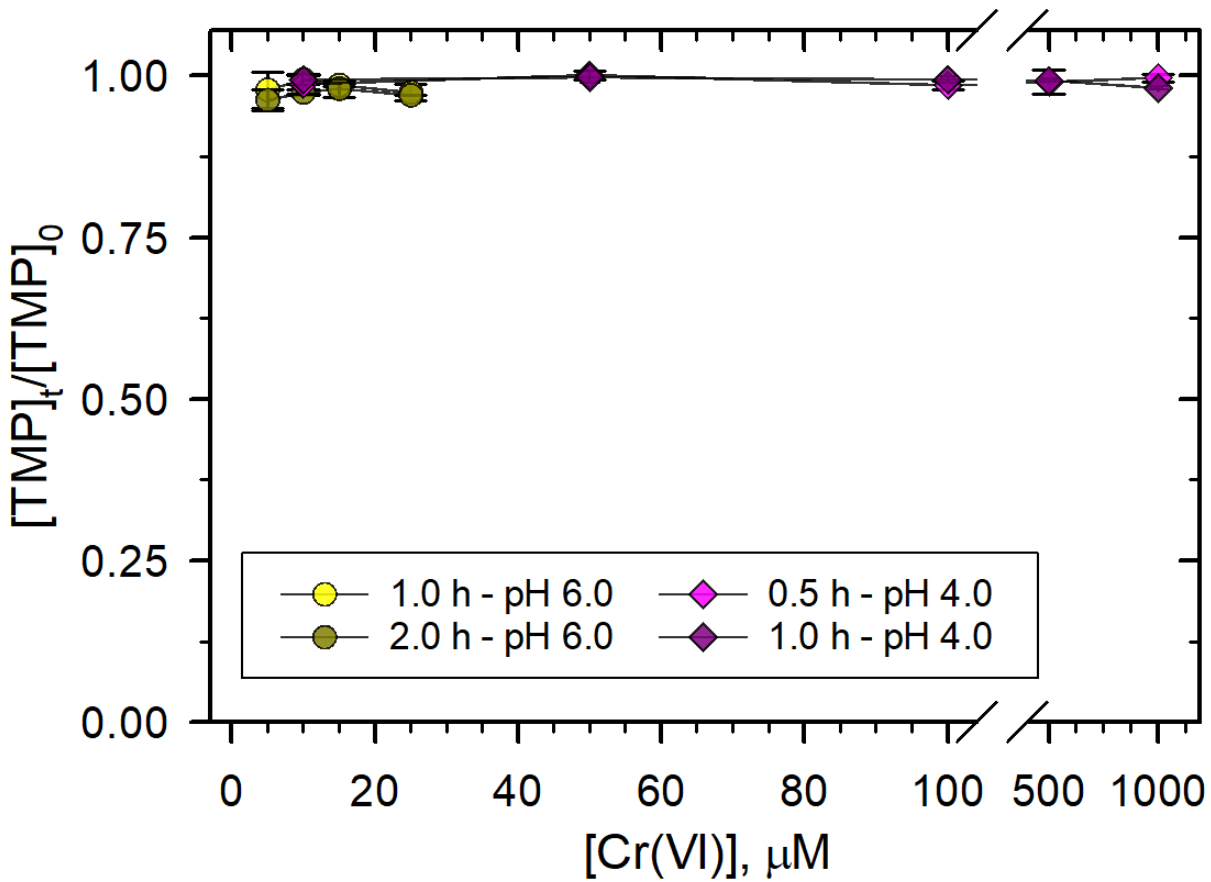
**Fig. 2.6.** Degradation of 5.0  $\mu\text{M}$  pollutants over 1.0 and 2.0 hours at pH 8.0 ( $[\text{Na}_2\text{HPO}_4] = 10.0$  mM) with  $[\text{Cr(III)}] = 263.0$   $\mu\text{M}$  and  $[\text{PAA}] = 1315$   $\mu\text{M}$ . (Abbreviations: ENR – enrofloxacin; TMP – trimethoprim; SMX – sulfamethoxazole; CBZ – carbamazepine; IBU – ibuprofen)



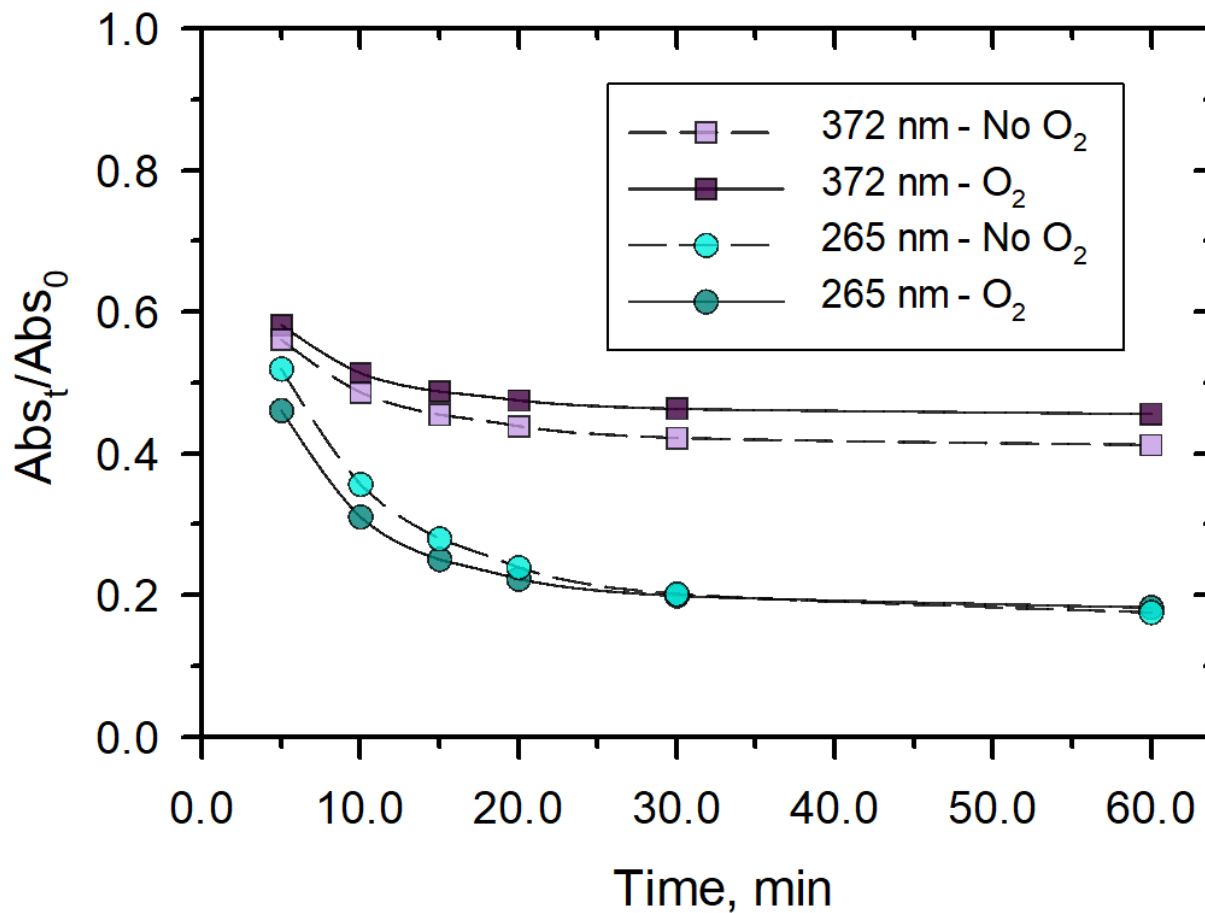
**Fig. 2.7.** UV-Visible spectra of mixing solution of PAA and Cr(III) at pH 8.0. (Experimental condition: [Cr(III)] = 100.0 μM; [PAA] = 500.0 – 5000.0 μM; [Na<sub>2</sub>HPO<sub>4</sub>] = 10.0 mM)



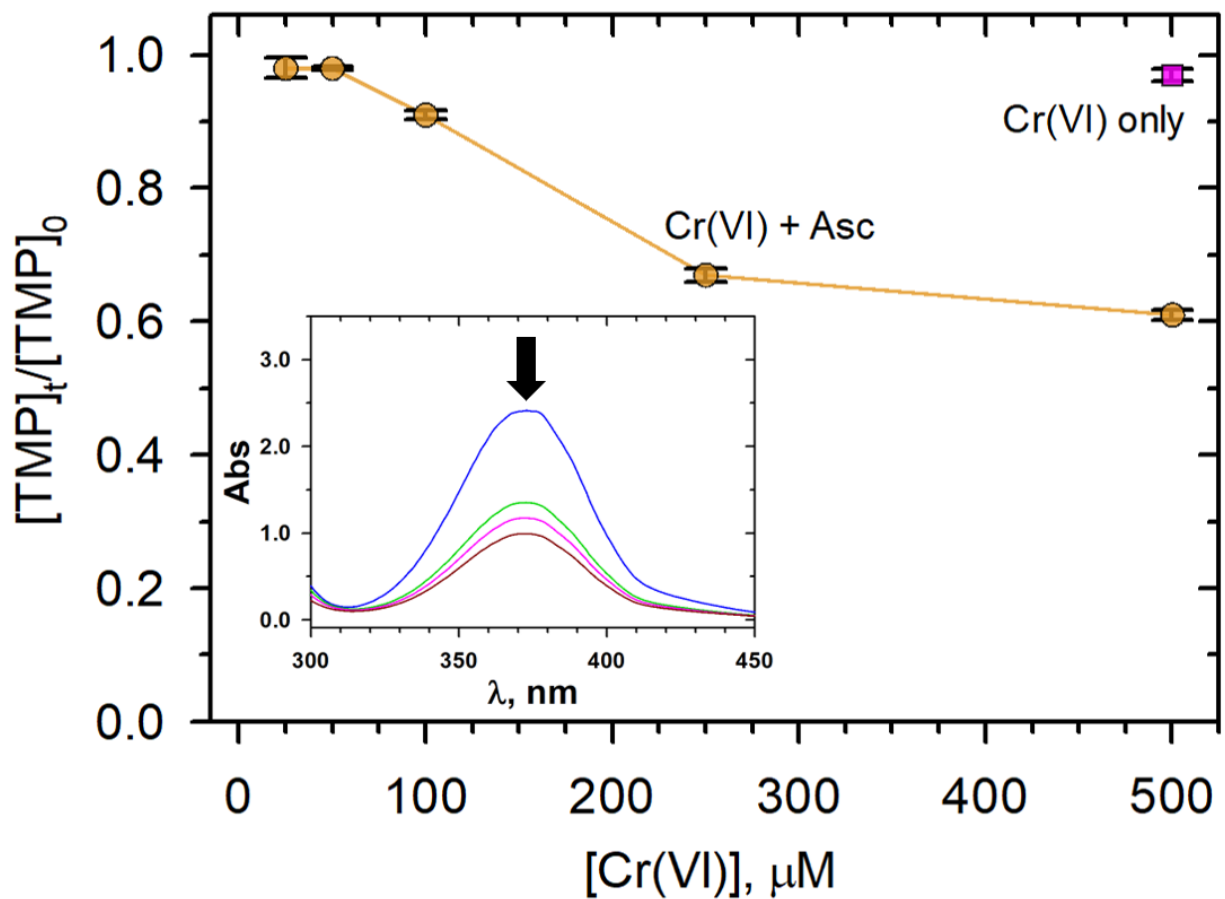
**Fig. 2.8.** UV-Visible spectra of Cr(VI)/PAA system at pH 8.0 indicating no significant change in Cr(VI) absorbance over 1.0 hour. (Experimental condition: [Cr(VI)] = 100.0  $\mu$ M; [PAA] = 500.0  $\mu$ M; [Na<sub>2</sub>HPO<sub>4</sub>] = 10.0 mM)



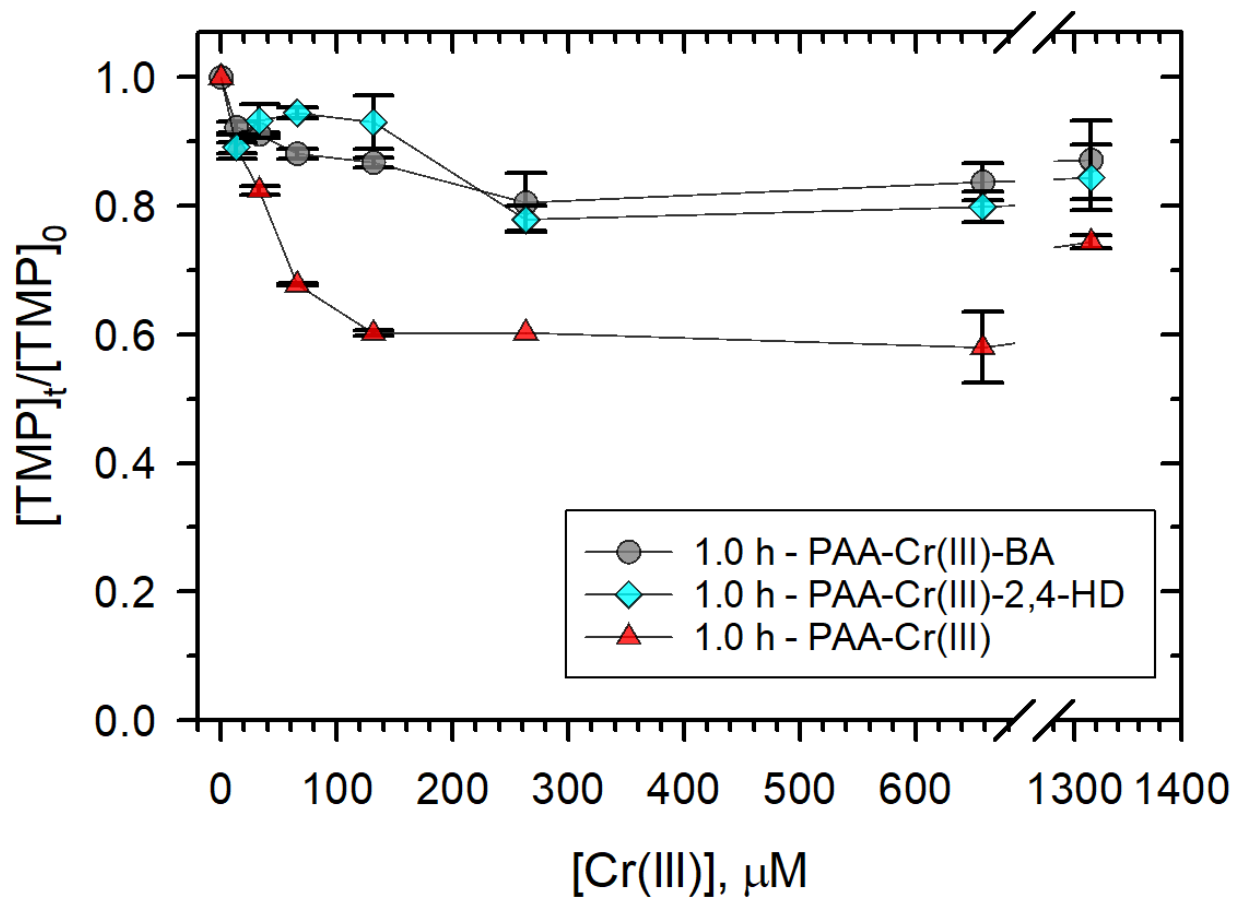
**Fig. 2.9.** Concentration of TMP in the mixed solution of TMP-Cr(VI)-PAA at pH 6.0 or 4.0 within 2.0 and 1.0 h, respectively. (Experimental conditions: [TMP] = 5.0 μM; [Cr(VI)] = 5.0 – 1000.0 μM; [PAA] = 100.0 μM; [Na<sub>2</sub>HPO<sub>4</sub>] = 10.0 mM)



**Fig. 2.10.** Change in UV-Visible absorbance of 500.0  $\mu\text{M}$  Cr(VI) and 500.0  $\mu\text{M}$  Asc at pH 7.0 ( $[\text{Na}_2\text{HPO}_4] = 10.0 \text{ mM}$ ) over 1.0 hour at 265 nm and 372 nm; indicating purging the system with  $\text{N}_2(\text{g})$  for 15 minutes had no significant impact on Asc oxidation or Cr(VI) reduction.

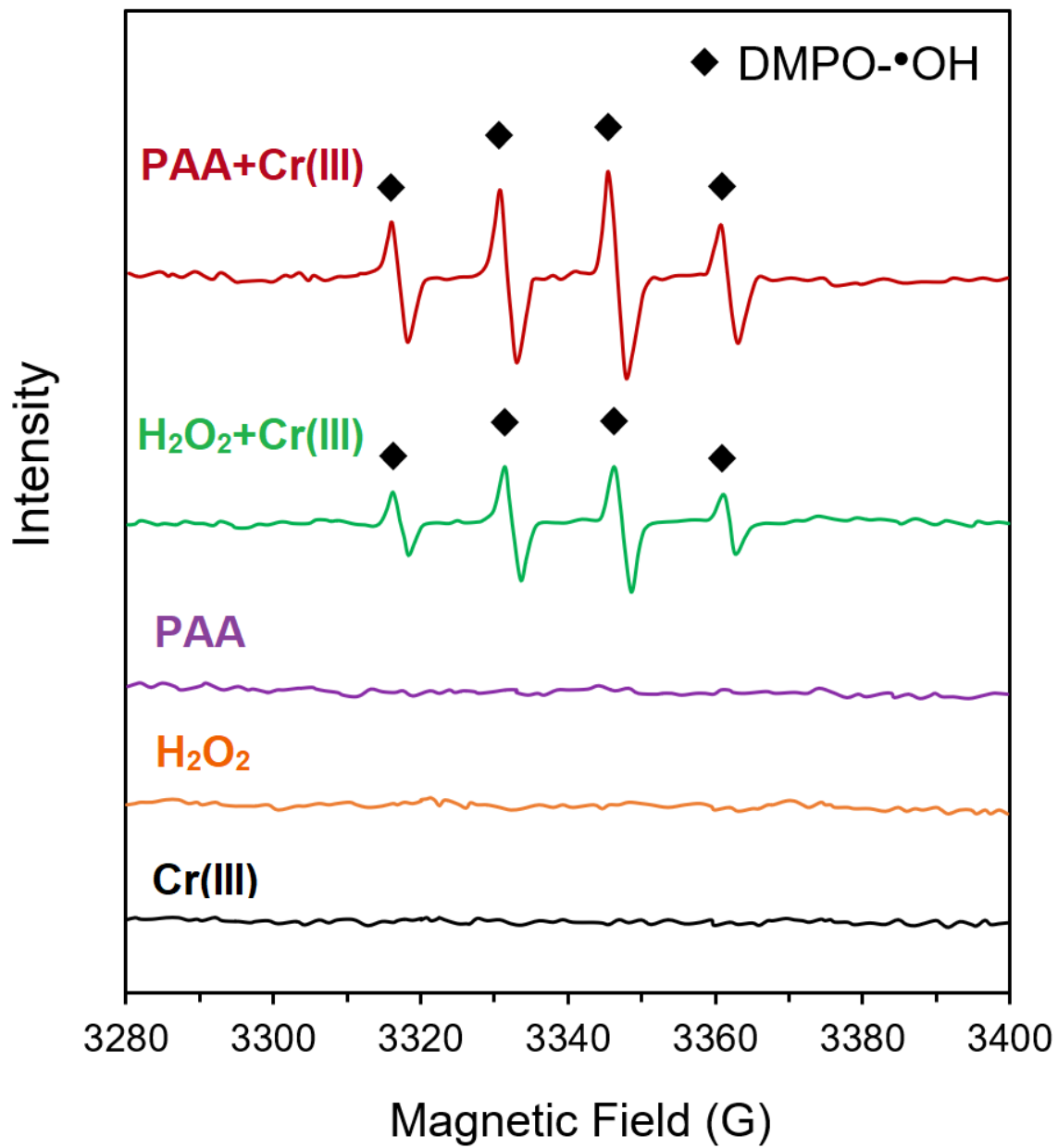


**Fig. 2.11.** Degradation of 5.0 TMP in 1.0 h at pH 7.0 ( $[Na_2HPO_4] = 10.0$  mM) in 500.0  $\mu M$  Asc and varying  $[Cr(VI)] = 25.0 - 500.0$   $\mu M$ . Inset of UV-visible absorbance showing a decrease in absorbance at 372 nm in 1.0 h under conditions of 500.0  $\mu M$  Cr(VI) and 500.0  $\mu M$  Asc at pH 7.0.

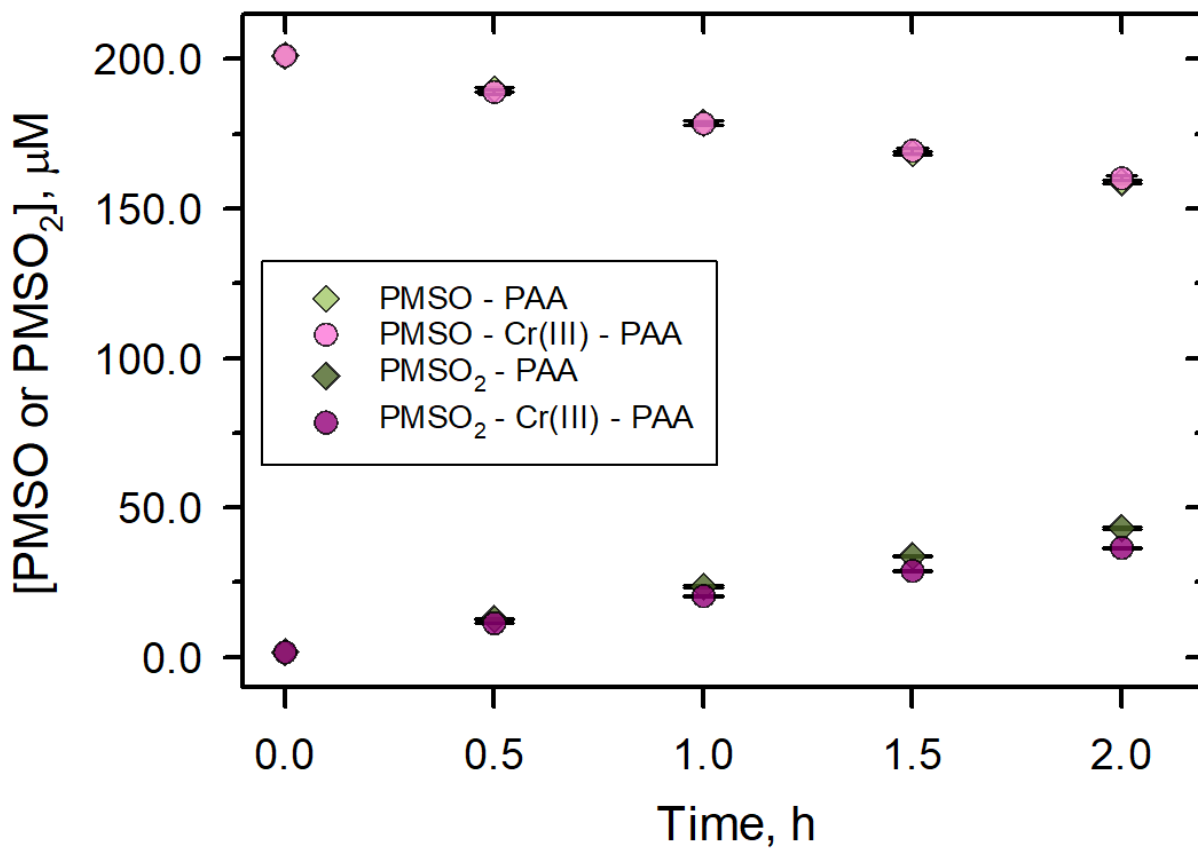


**Fig. 2.12.** Degradation of TMP in PAA-Cr(III) system at pH 8.0 indicating quenching of the  $\bullet\text{OH}$  yet a negligible detection of PAA radicals. (Experimental conditions:  $[\text{TMP}] = 5.0 \mu\text{M}$ ;  $[\text{Cr(III)}] = 13.15 - 1315 \mu\text{M}$ ;  $[\text{PAA}] = 1315 \mu\text{M}$ ;  $[\text{BA}] = 13.16 \text{ mM}$ ;  $[\text{2,4-HD}] = 5.0 \text{ mM}$ ;  $[\text{Na}_2\text{HPO}_4] = 10.0 \text{ mM}$ )





**Fig. 2.13.** EPR spectra of DMPO-•OH indicating presence of •OH in both PAA-Cr(III) and H<sub>2</sub>O<sub>2</sub>-Cr(III) systems at pH 8.0. (Experimental conditions: [Cr(III)] = 263.0 μM; [H<sub>2</sub>O<sub>2</sub>] = 520.5 μM; [PAA] = 1315 μM; [DMPO] = 50.0 mM; [Na<sub>2</sub>HPO<sub>4</sub>] = 10.0 mM).



**Fig. 2.14.** Oxidation of 200.0 μM PMSO to PMSO<sub>2</sub> in 2.0 hours by 1315 μM PAA alone and with 263.0 μM Cr(III) at pH 8.0 ([Na<sub>2</sub>HPO<sub>4</sub>] = 10.0 mM).

## 2.6. References

- (1) Kim, J.; Huang, C.-H. Reactivity of Peracetic Acid with Organic Compounds: A Critical Review. *ACS EST Water* **2021**, *1* (1), 15–33. <https://doi.org/10.1021/acsestwater.0c00029>.
- (2) Zhang, T.; Wang, T.; Mejia-Tickner, B.; Kissel, J.; Xie, X.; Huang, C.-H. Inactivation of Bacteria by Peracetic Acid Combined with Ultraviolet Irradiation: Mechanism and Optimization. *Environ. Sci. Technol.* **2020**, *54* (15), 9652–9661. <https://doi.org/10.1021/acs.est.0c02424>.
- (3) Sharma, N.; Bhardwaj, N. K.; Singh, R. B. P. Environmental Issues of Pulp Bleaching and Prospects of Peracetic Acid Pulp Bleaching: A Review. *J. Clean. Prod.* **2020**, *256*, 120338. <https://doi.org/10.1016/j.jclepro.2020.120338>.
- (4) Lee, W.-N.; Huang, C.-H. Formation of Disinfection Byproducts in Wash Water and Lettuce by Washing with Sodium Hypochlorite and Peracetic Acid Sanitizers. *Food Chem. X* **2019**, *1*, 100003. <https://doi.org/10.1016/j.fochx.2018.100003>.
- (5) Kim, J.; Zhang, T.; Liu, W.; Du, P.; Dobson, J. T.; Huang, C.-H. Advanced Oxidation Process with Peracetic Acid and Fe(II) for Contaminant Degradation. *Environ. Sci. Technol.* **2019**, *53* (22), 13312–13322. <https://doi.org/10.1021/acs.est.9b02991>.
- (6) Kim, J.; Du, P.; Liu, W.; Luo, C.; Zhao, H.; Huang, C.-H. Cobalt/Peracetic Acid: Advanced Oxidation of Aromatic Organic Compounds by Acetylperoxyl Radicals. *Environ. Sci. Technol.* **2020**, *54* (8), 5268–5278. <https://doi.org/10.1021/acs.est.0c00356>.
- (7) Li, R.; Manoli, K.; Kim, J.; Feng, M.; Huang, C.-H.; Sharma, V. K. Peracetic Acid–Ruthenium(III) Oxidation Process for the Degradation of Micropollutants in Water. *Environ. Sci. Technol.* **2021**, *55* (13), 9150–9160. <https://doi.org/10.1021/acs.est.0c06676>.

- (8) Manoli, K.; Li, R.; Kim, J.; Feng, M.; Huang, C.-H.; Sharma, V. K. Ferrate(VI)-Peracetic Acid Oxidation Process: Rapid Degradation of Pharmaceuticals in Water. *Chem. Eng. J.* **2022**, *429*, 132384. <https://doi.org/10.1016/j.cej.2021.132384>.
- (9) Choppala, G.; Bolan, N.; Park, J. H. Chapter Two - Chromium Contamination and Its Risk Management in Complex Environmental Settings. In *Advances in Agronomy*; Sparks, D. L., Ed.; Academic Press, 2013; Vol. 120, pp 129–172. <https://doi.org/10.1016/B978-0-12-407686-0.00002-6>.
- (10) Deng, Y.; Wang, M.; Tian, T.; Lin, S.; Xu, P.; Zhou, L.; Dai, C.; Hao, Q.; Wu, Y.; Zhai, Z.; Zhu, Y.; Zhuang, G.; Dai, Z. The Effect of Hexavalent Chromium on the Incidence and Mortality of Human Cancers: A Meta-Analysis Based on Published Epidemiological Cohort Studies. *Front. Oncol.* **2019**, *9*, 24. <https://doi.org/10.3389/fonc.2019.00024>.
- (11) Eastmond, D. A.; MacGregor, J. T.; Slesinski, R. S. Trivalent Chromium: Assessing the Genotoxic Risk of an Essential Trace Element and Widely Used Human and Animal Nutritional Supplement. *Crit. Rev. Toxicol.* **2008**, *38* (3), 173–190. <https://doi.org/10.1080/10408440701845401>.
- (12) Pradhan, D.; Sukla, L. B.; Sawyer, M.; Rahman, P. K. S. M. Recent Bioreduction of Hexavalent Chromium in Wastewater Treatment: A Review. *J. Ind. Eng. Chem.* **2017**, *55*, 1–20. <https://doi.org/10.1016/j.jiec.2017.06.040>.
- (13) Owlad, M.; Aroua, M. K.; Daud, W. A. W.; Baroutian, S. Removal of Hexavalent Chromium-Contaminated Water and Wastewater: A Review. *Water. Air. Soil Pollut.* **2009**, *200* (1–4), 59–77. <https://doi.org/10.1007/s11270-008-9893-7>.

- (14) Chen, Q. Y.; Murphy, A.; Sun, H.; Costa, M. Molecular and Epigenetic Mechanisms of Cr(VI)-Induced Carcinogenesis. *Toxicol. Appl. Pharmacol.* **2019**, *377*, 114636. <https://doi.org/10.1016/j.taap.2019.114636>.
- (15) Barrera-Díaz, C. E.; Lugo-Lugo, V.; Bilyeu, B. A Review of Chemical, Electrochemical and Biological Methods for Aqueous Cr(VI) Reduction. *J. Hazard. Mater.* **2012**, *223–224*, 1–12. <https://doi.org/10.1016/j.jhazmat.2012.04.054>.
- (16) Xia, S.; Song, Z.; Jeyakumar, P.; Shaheen, S. M.; Rinklebe, J.; Ok, Y. S.; Bolan, N.; Wang, H. A Critical Review on Bioremediation Technologies for Cr(VI)-Contaminated Soils and Wastewater. *Crit. Rev. Environ. Sci. Technol.* **2019**, *49* (12), 1027–1078. <https://doi.org/10.1080/10643389.2018.1564526>.
- (17) Bhati, A.; Anand, S. R.; Saini, D.; Gunture; Sonkar, S. K. Sunlight-Induced Photoreduction of Cr(VI) to Cr(III) in Wastewater by Nitrogen-Phosphorus-Doped Carbon Dots. *Npj Clean Water* **2019**, *2* (1), 12. <https://doi.org/10.1038/s41545-019-0036-z>.
- (18) Chebeir, M.; Liu, H. Oxidation of Cr(III)–Fe(III) Mixed-Phase Hydroxides by Chlorine: Implications on the Control of Hexavalent Chromium in Drinking Water. *Environ. Sci. Technol.* **2018**, *52* (14), 7663–7670. <https://doi.org/10.1021/acs.est.7b06013>.
- (19) Bokare, A. D.; Choi, W. Advanced Oxidation Process Based on the Cr(III)/Cr(VI) Redox Cycle. *Environ. Sci. Technol.* **2011**, *45* (21), 9332–9338. <https://doi.org/10.1021/es2021704>.
- (20) Houshyar, Z.; Khoshfetrat, A. B.; Fatehifar, E. Influence of Ozonation Process on Characteristics of Pre-Alkalinized Tannery Effluents. *Chem. Eng. J.* **2012**, *191*, 59–65. <https://doi.org/10.1016/j.cej.2012.02.053>.

- (21) Bell, J.; Ma, X.; McDonald, T. J.; Huang, C.-H.; Sharma, V. K. Overlooked Role of Chromium(V) and Chromium(IV) in Chromium Redox Reactions of Environmental Importance. *Environ. Sci. Technol. Water* **2021**, Submitted.
- (22) Dong, H.; Wei, G.; Cao, T.; Shao, B.; Guan, X.; Strathmann, T. J. Insights into the Oxidation of Organic Cocontaminants during Cr(VI) Reduction by Sulfite: The Overlooked Significance of Cr(V). *Environ. Sci. Technol.* **2020**, *54* (2), 1157–1166. <https://doi.org/10.1021/acs.est.9b03356>.
- (23) Bokare, A. D.; Choi, W. Chromate-Induced Activation of Hydrogen Peroxide for Oxidative Degradation of Aqueous Organic Pollutants. *Environ. Sci. Technol.* **2010**, *44* (19), 7232–7237. <https://doi.org/10.1021/es903930h>.
- (24) Jelic, A.; Gros, M.; Ginebreda, A.; Cespedes-Sánchez, R.; Ventura, F.; Petrovic, M.; Barcelo, D. Occurrence, Partition and Removal of Pharmaceuticals in Sewage Water and Sludge during Wastewater Treatment. *Water Res.* **2011**, *45* (3), 1165–1176. <https://doi.org/10.1016/j.watres.2010.11.010>.
- (25) Wang, J.; Chu, L.; Wojnárovits, L.; Takács, E. Occurrence and Fate of Antibiotics, Antibiotic Resistant Genes (ARGs) and Antibiotic Resistant Bacteria (ARB) in Municipal Wastewater Treatment Plant: An Overview. *Sci. Total Environ.* **2020**, *744*, 140997. <https://doi.org/10.1016/j.scitotenv.2020.140997>.
- (26) Anquandah, G. A. K.; Sharma, V. K.; Knight, D. A.; Batchu, S. R.; Gardinali, P. R. Oxidation of Trimethoprim by Ferrate(VI): Kinetics, Products, and Antibacterial Activity. *Environ. Sci. Technol.* **2011**, *45* (24), 10575–10581. <https://doi.org/10.1021/es202237g>.
- (27) Rizzo, L.; Manaia, C.; Merlin, C.; Schwartz, T.; Dagot, C.; Ploy, M. C.; Michael, I.; Fatta-Kassinos, D. Urban Wastewater Treatment Plants as Hotspots for Antibiotic Resistant

- Bacteria and Genes Spread into the Environment: A Review. *Sci. Total Environ.* **2013**, *447*, 345–360. <https://doi.org/10.1016/j.scitotenv.2013.01.032>.
- (28) Bijlsma, L.; Pitarch, E.; Fonseca, E.; Ibáñez, M.; Botero, A. M.; Claros, J.; Pastor, L.; Hernández, F. Investigation of Pharmaceuticals in a Conventional Wastewater Treatment Plant: Removal Efficiency, Seasonal Variation and Impact of a Nearby Hospital. *J. Environ. Chem. Eng.* **2021**, *9* (4), 105548. <https://doi.org/10.1016/j.jece.2021.105548>.
- (29) Le, T.-H.; Ng, C.; Tran, N. H.; Chen, H.; Gin, K. Y.-H. Removal of Antibiotic Residues, Antibiotic Resistant Bacteria and Antibiotic Resistance Genes in Municipal Wastewater by Membrane Bioreactor Systems. *Water Res.* **2018**, *145*, 498–508. <https://doi.org/10.1016/j.watres.2018.08.060>.
- (30) Anjali, R.; Shanthakumar, S. Insights on the Current Status of Occurrence and Removal of Antibiotics in Wastewater by Advanced Oxidation Processes. *J. Environ. Manage.* **2019**, *246*, 51–62. <https://doi.org/10.1016/j.jenvman.2019.05.090>.
- (31) Ji, Y.; Xie, W.; Fan, Y.; Shi, Y.; Kong, D.; Lu, J. Degradation of Trimethoprim by Thermo-Activated Persulfate Oxidation: Reaction Kinetics and Transformation Mechanisms. *Chem. Eng. J.* **2016**, *286*, 16–24. <https://doi.org/10.1016/j.cej.2015.10.050>.
- (32) Masters, P. A.; O'Bryan, T. A.; Zurlo, J.; Miller, D. Q.; Joshi, N. Trimethoprim-Sulfamethoxazole Revisited. *Arch. Intern. Med.* **2003**, *163* (4), 402–410. <https://doi.org/10.1001/archinte.163.4.402>.
- (33) Qiang, Z.; Adams, C. Potentiometric Determination of Acid Dissociation Constants (PKa) for Human and Veterinary Antibiotics. *Water Res.* **2004**, *38* (12), 2874–2890. <https://doi.org/10.1016/j.watres.2004.03.017>.

- (34) Roth, B.; Strelitz, J. Z. Protonation of 2, 4-Diaminopyrimidines. I. Dissociation Constants and Substituent Effects. *J. Org. Chem.* **1969**, *34* (4), 821–836.
- (35) Rai, D.; Sass, B. M.; Moore, D. A. Chromium (III) Hydrolysis Constants and Solubility of Chromium (III) Hydroxide. *Inorg. Chem.* **1987**, *26* (3), 345–349.
- (36) Goodgame, D. M. L.; Joy, A. M. EPR Study of the Cr(V) and Radical Species Produced in the Reduction of Cr(VI) by Ascorbate. *Inorganica Chim. Acta* **1987**, *135* (2), 115–118.  
[https://doi.org/10.1016/S0020-1693\(00\)83273-9](https://doi.org/10.1016/S0020-1693(00)83273-9).
- (37) Zhang, L.; Lay, P. A. EPR Spectroscopic Studies of the Reactions of Cr(VI) with L - Ascorbic Acid, L -Dehydroascorbic Acid, and 5,6- O -Isopropylidene- L -Ascorbic Acid in Water. <sup>1</sup> Implications for Chromium(VI) Genotoxicity. *J. Am. Chem. Soc.* **1996**, *118* (50), 12624–12637. <https://doi.org/10.1021/ja961824c>.
- (38) Du, J.; Cullen, J. J.; Buettner, G. R. Ascorbic Acid: Chemistry, Biology and the Treatment of Cancer. *Biochim. Biophys. Acta BBA - Rev. Cancer* **2012**, *1826* (2), 443–457.  
<https://doi.org/10.1016/j.bbcan.2012.06.003>.
- (39) Bielski, B. H. Chemistry of Ascorbic Acid Radicals; ACS Publications, 1982.
- (40) Mortensen, A. Scavenging of Acetylperoxyl Radicals and Quenching of Triplet Diacetyl by  $\beta$ -Carotene: Mechanisms and Kinetics. *J. Photochem. Photobiol. B* **2001**, *61* (1–2), 62–67. [https://doi.org/10.1016/S1011-1344\(01\)00146-4](https://doi.org/10.1016/S1011-1344(01)00146-4).
- (41) Grosjean, D.; Williams, E. L. Environmental Persistence of Organic Compounds Estimated from Structure-Reactivity and Linear Free-Energy Relationships. Unsaturated Aliphatics. *Atmospheric Environ. Part Gen. Top.* **1992**, *26* (8), 1395–1405.  
[https://doi.org/10.1016/0960-1686\(92\)90124-4](https://doi.org/10.1016/0960-1686(92)90124-4).



- (42) Wu, C.; De Visscher, A.; Gates, I. D. Reactions of Hydroxyl Radicals with Benzoic Acid and Benzoate. *RSC Adv.* **2017**, *7* (57), 35776–35785.  
<https://doi.org/10.1039/C7RA05488B>.
- (43) Zong, Y.; Zhang, H.; Zhang, X.; Shao, Y.; Zeng, Y.; Ji, W.; Xu, L.; Wu, D. Highly Selective Oxidation of Organic Contaminants in the RuIII-Activated Peroxymonosulfate Process: The Dominance of RuVO Species. *Chemosphere* **2021**, *285*, 131544.  
<https://doi.org/10.1016/j.chemosphere.2021.131544>.
- (44) Zong, Y.; Guan, X.; Xu, J.; Feng, Y.; Mao, Y.; Xu, L.; Chu, H.; Wu, D. Unraveling the Overlooked Involvement of High-Valent Cobalt-Oxo Species Generated from the Cobalt(II)-Activated Peroxymonosulfate Process. *Environ. Sci. Technol.* **2020**, *54* (24), 16231–16239. <https://doi.org/10.1021/acs.est.0c06808>.
- (45) Richard, F. C.; Bourg, A. C. M. Aqueous Geochemistry of Chromium: A Review. *Water Res.* **1991**, *25* (7), 807–816. [https://doi.org/10.1016/0043-1354\(91\)90160-R](https://doi.org/10.1016/0043-1354(91)90160-R).

## CHAPTER 3

### Conclusions and perspectives

Environmental ubiquity of chromium, its industrial applications, and varying toxicity based on oxidation state give reason to the continued interest in this widespread element. Toxicity studies under biological environments clearly suggest the role of high-valent Cr(V) and Cr(IV) species.<sup>1</sup> Comparatively, roles of such intermediate Cr species in environmental processes and exploration of their potential uses in redox reactions of Cr is lacking greatly. Chapter 1 provides fundamental knowledge known for Cr(V) and Cr(IV) in aquatic environments to guide researchers to characterize them using spectroscopic methods such as UV-visible and EPR techniques and subsequently perform mechanistic evaluation of the redox system. Additionally, examples presented on various redox reactions of Cr may assist in designing the experiments to evaluate potential of Cr(V) and/or Cr(IV) species in the environmental systems of interest. Furthermore, formation of Cr(V) and Cr(IV) during the interaction of Cr(VI)/Cr(III) with functionalities of NOM needs further in-depth investigations to learn their role in various natural and engineered processes including decontamination of organic contaminants.

With the rise of popularity in use of PAA in wastewater treatment, it becomes important to analyze potential inadvertent mechanisms in the water matrix. The research presented in Chapter 2 systematically investigated the kinetics and mechanism to learn if the interaction of Cr(III) and PAA occurred under the conditions relevant to wastewater treatment. The interaction produced reactive species that could degrade a wide range of coexisting organic pollutants present in water. Degradation of organic pollutants depended on their molecular structure. Reactive species in this system responsible for the degradation of pollutants were •OH radicals

and Cr(IV)/Cr(V) species, which were confirmed by chemical probes in degradation kinetics, UV-visible, and EPR spectroscopy measurements. The results also showed the formation of Cr(VI) through the interaction of Cr(III) and PAA under certain conditions.

It is possible that Cr(III) from may enter wastewater treatment posing two primary implications: formation of undesired Cr(VI) and degradation of recalcitrant organic contaminants. Moreover, just as residual chlorine has shown to oxidize Cr(0) and/or Cr(III) to Cr(VI) in drinking water distribution pipes, PAA may function in a similar fashion.<sup>2,3</sup> Notably, implementation of Cr(III) to activate PAA is not recommended because of potentially formed Cr(VI) in wastewater that would require additional treatment to remediate it. Future studies may look at how PAA could oxidize Cr(0) existing in iron corrosion scales from drinking water pipes. This may add insight to the disadvantages of such a promising disinfectant.

The presented research herein advances scientific understanding on PAA activation by metal ions, the potential of Cr(IV) and Cr(V) in pollutant degradation, and on mechanisms for possible undesirable production of Cr(VI) under certain environmental conditions.

### 3.1 References

- (1) Levina, A.; Lay, P. A. Mechanistic Studies of Relevance to the Biological Activities of Chromium. *Coordination Chemistry Reviews* **2005**, *249* (3–4), 281–298.  
<https://doi.org/10.1016/j.ccr.2004.02.017>.
- (2) Chebeir, M.; Liu, H. Oxidation of Cr(III)–Fe(III) Mixed-Phase Hydroxides by Chlorine: Implications on the Control of Hexavalent Chromium in Drinking Water. *Environ. Sci. Technol.* **2018**, *52* (14), 7663–7670. <https://doi.org/10.1021/acs.est.7b06013>.
- (3) Tan, C.; Avasarala, S.; Liu, H. Hexavalent Chromium Release in Drinking Water Distribution Systems: New Insights into Zerovalent Chromium in Iron Corrosion Scales. *Environ. Sci. Technol.* **2020**, *54* (20), 13036–13045.  
<https://doi.org/10.1021/acs.est.0c03922>.